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Carbon and nitrogen relations in surface and subsurface marine sediments*

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(*Received* 10 *November* 1954)

ABSTRACT

The carbon and nitrogen content of marine sediments is associated with processes such as rates of sedimentation, and environmental aspects of deposition and diagenesis. Information on the distribution of these elements is also pertinent to the evaluation and reconstruction of past environments. It is thus necessary that we have a more thorough understanding of the relationship between carbon and nitrogen in sedimentary materials.

The logarithmic relationship of carbon and nitrogen for sixty-five samples of near-shore marine sediments, both surface and subsurface, has been examined. The results are compared, using data from various sources. Carbon and nitrogen show an approximately logarithmic linear functional relation. For both surface and subsurface samples the statistical C/N ratio may increase or decrease with increasing organic content. The slopes of the least-squares lines, representing this relationship, range from 0·09 to the vertical. Sediments obtained from a Maine fjord indicate that the carbon-nitrogen association for surface and subsurface samples are quite different. The organic supply and environment of organic decomposition appear to be the primary factors controlling the ratio of carbon to nitrogen loss. The particular type of relationship between carbon and nitrogen in marine sediments varies considerably. Consequently data from different areas must be treated separately.

Introduction

In the many studies of marine sedimentary organics, emphasis is placed upon the carbon-nitrogen ratio. Trask (1932), Waksman (1933), Grippenberg (1934), Wiseman and Bennett (1940), Mohamed (1949), and Arrhenius (1950) are but a few of the contributors to information concerning the carbon-nitrogen relationship in marine sediments. The general consensus of opinion, as pointed out by Arrhenius, is that the source of the organic matter is the major factor to consider. He then expressed a personal opinion that mineral matter dilution may quantitatively affect the microbiological decomposition, thus becoming the controlling factor with respect to carbon and nitrogen concentrations. The varying concentrations of lignin in modern marine sediments as shown by Bader (1954) may well have some controlling aspect on the carbon-nitrogen ratio. This, when considering the lignin studies of Waksman and Irye (1932) and Fuller and Norman (1943), is probably dependent upon the formation of stable ligno-protein complexes.

In view of the variations in the data and opinions of other investigators, all information on the relationship between carbon and nitrogen in sedimentary material is of value. Additional data may assist in understanding some of the details concerning the role of organic matter in the sedimentary diagenetic processes, and its usefulness in paleo-ecologic reconstructions. The origional carbon and nitrogen data presented in this paper were obtained from a total of sixty-five marine sediment samples from the near-shore regions of the Gulf of Maine and Puget Sound. Forty-three samples represent surface sediments, while twenty-two are subsurface samples from thirteen cores. The organic carbon content was

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determined by a semimicro dry combustion method, the carbon from carbonates being previously removed from the sample by acidifying the sample with warm dilute HCl. Briefly, the analysis consisted of combusting a powdered sample of known weight in a measured volume of oxygen under controlled pressure. The evolved carbon was calculated from the gravimetrically determined CO_2. The nitrogen content was obtained by the standard micro-Kjeldahl method.

Carbon and Nitrogen in Surface Sediments

The carbon concentrations in the forty-four surface samples ranged from 4·74 per cent to 0·24 per cent, with a mean of 1·61 per cent. The nitrogen content varied between 0·58 per cent and 0·02 per cent, the mean being 0·19 per cent. In order to readily compare these data with those of other published studies, the carbon and nitrogen relationships are presented in Fig. 1 on a logarithmic basis. These two variables apparently have an approximate logarithmic linear functional relation. The slope of the least-squares line is about 0·91. This indicates a slight statistical decrease in the C/N ratio with increasing organics. The data (Table 1) shows, however, that individually the C/N ratio may deviate widely from the statistical mean.

In comparing the statistical line as shown in Fig. 1 with some of the published information there is both close correspondence and wide variation. Fig. 2 compares the data of various authors as given by Arrhenius (1950). The data of this

Table 1. *Carbon and nitrogen in surface samples*

Sample No.	% *Carbon*	% *Nitrogen*	*C/N*	*Sample No.*	% *Carbon*	% *Nitrogen*	*C/N*
1	0·88	0·14	6·2	23	1·82	0·20	9·1
2	1·72	0·22	7·8	24	0·34	0·05	6·8
3	0·52	0·05	10·4	25	0·30	0·04	7·5
4	1·24	0·11	11·1	26	1·96	0·15	13·1
5	0·94	0·13	6·2	27	2·13	0·17	12·5
6	0·42	0·03	14·0	28	1·86	0·18	10·3
7	0·45	0·02	22·5	29	2·12	0·29	7·3
8	0·66	0·10	6·6	30	2·34	0·26	9·0
9	1·02	0·04	25·5	31	1·78	0·21	8·5
10	0·46	0·03	15·3	32	0·26	0·03	8·6
11	0·35	0·04	8·7	33	1·38	0·07	19·7
12	1·74	0·28	6·2	34	0·34	0·03	11·3
13	1·15	0·14	8·2	35	0·87	0·35	2·5
14	0·49	0·06	8·2	36	3·17	0·25	12·7
15	4·12	0·36	11·4	37	0·24	0·02	12·0
16	4·74	0·49	9·7	38	3·90	0·40	9·7
17	4·12	0·40	10·3	39	0·95	0·13	7·3
18	3·12	0·50	6·2	40	0·29	0·03	9·7
19	2·97	0·58	5·1	41	1·02	0·09	10·3
20	2·66	0·33	8·1	42	1·96	0·22	7·9
21	2·94	0·35	8·4	43	1·62	0·19	8·5
22	2·11	0·29	6·3				

investigation corresponds closely with that of Waksman (1933) and Grippenberg (1934). The approximate slope of the mean line calculated from Waksman's data is 1·11; the slope of the line derived from Grippenberg's analyses is about 0·86. The former illustrates a slight increase in C/N ratio with increasing organics,

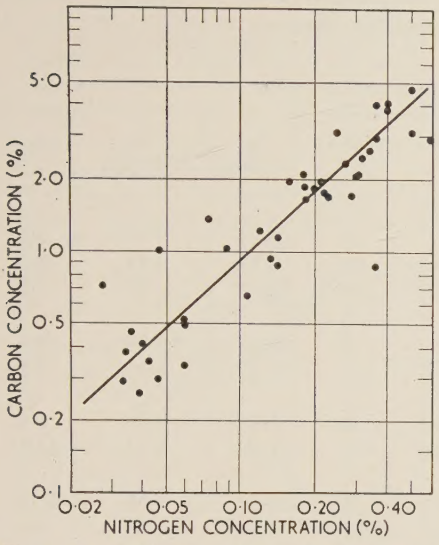

Fig. 1. Logarithmic carbon-nitrogen relations for surface sediment samples from the Gulf of Maine and Puget Sound.

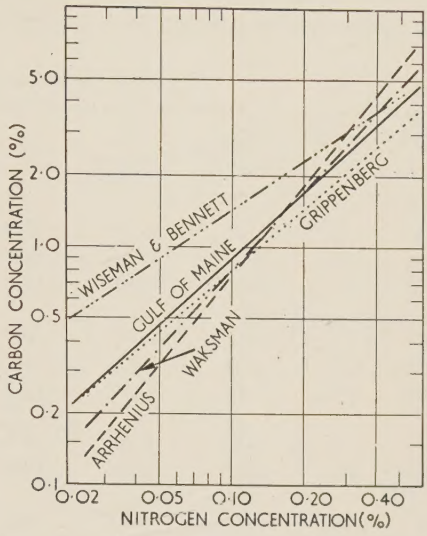

Fig. 2. Comparison of statistical relations of logarithmic carbon and nitrogen concentrations in marine sediments. The data from various sources have been treated individually.

the latter a decrease. The 417 pairs of analyses plotted by Arrhenius (1950) indicate an approximate slope of 1·28. These, and especially the Wiseman and Bennett data (slope of 0·67), differ the most from the surface samples analyzed for this study.

Carbon and Nitrogen in Subsurface Sediments

In conjunction with the surface sample investigation, the carbon and nitrogen concentrations were determined at various subsurface levels in thirteen cores. Core samples 15 through 23 (Table 2) represent a single fjord environment off the coast of Maine. Cores 41 through 44 (Table 2) were taken in Puget Sound.

Fig. 3 illustrates the carbon-nitrogen relations as expressed logarithmically for the Maine fjord samples. The points representing the surface and subsurface samples for each core are connected by a line. The point on the extreme right for each core represents the surface sample; each succeeding subsurface sample decreases in carbon and nitrogen. From this figure and the table it can be seen that there is an uninterrupted decrease in the organic material with increasing depth. The particle size characteristics of the inorganic fraction are constant throughout each core with median diameters of about 0·007 mm. In view of the location of the samples, the uniformity of inorganic particle size and the steadily decreasing organic concentrations, it may be assumed that radical depositional environment changes have probably not occurred in the time represented by the samples. The

slopes of the lines representing the logarithmic functional relationship of carbon and nitrogen for each core range from 0·09 to 0·72, with a mean of 0·36.

Fig. 4 compares the Maine fjord surface and subsurface samples. The line of best fit for the twelve surface samples in the fjord is essentially the same as the established line for all Gulf of Maine samples as given in Fig. 1. The difference in slope between the surface and subsurface samples is obvious.

Table 2. Carbon and nitrogen in core samples

Sample No.	*Depth (cm)*	*% Carbon*	*% Nitrogen*	*C/N*	*Sample No.*	*Depth (cm)*	*% Carbon*	*% Nitrogen*	*C/N*
15	0	4·13	0·36	11·4	21	0	2·94	0·35	8·4
15a	20	2·84	0·20	14·2	21a	20	2·77	0·34	8·1
15b	47	2·66	0·16	16·6	21b	50	2·54	0·29	8·8
16	0	4·74	0·49	9·7	22	0	2·11	0·29	6·3
16a	20	4·54	0·28	16·2	22a	40	1·97	0·24	8·2
16b	42	4·42	0·24	18·4					
					23	0	1·82	0·20	9·1
17	0	4·12	0·40	10·3	23a	37	1·56	0·14	11·1
17a	46	3·63	0·26	14·0					
					41	0	1·02	0·09	11·3
18	0	3·12	0·50	6·2	41a	115	0·74	0·08	9·3
18a	39	2·70	0·35	7·7	41b	213	0·78	0·08	9·7
19	0	2·97	0·58	5·1	42	0	1·96	0·22	8·9
19a	9	2·62	0·45	5·8	42a	8	1·56	0·22	7·1
19b	42	2·44	0·31	7·9	42b	74	2·38	0·23	10·3
					42c	150	2·00	0·22	9·1
20	0	2·66	0·33	8·1					
20a	20	2·58	0·20	12·9	43	0	1·62	0·19	8·5
20b	30	2·59	0·26	9·9	43a	26	1·35	0·17	7·9
					44a	155	2·19	0·23	9·5
					44b	246	1·11	0·21	5·3

The core samples from Puget Sound are indicative of diverse environmental conditions with time. This is shown by marked particle size variations and abrupt changes in the organic content at various depths in the cores. The situation in this area is thus more complex than in the Maine fjord. The slopes of the lines representing the logarithmic functional relationship of carbon and nitrogen for each core range from 1·80 to the vertical, with a mean of 3·49.

In order to further illustrate the complexity of the situation, the results of other investigations are included. In some instances the carbon-nitrogen relations with depth were not directly considered by the authors. The subsurface data from the Gulf of Maine area and Puget Sound are presented in Fig. 5 and compared with information from the following four sources:

Trask (1932) presented data on the carbon and nitrogen in some cores from the

Channel Islands off the coast of California. By plotting the logarithmic carbon and nitrogen relations for eighteen cores it was found that the slopes of the resulting lines arranged themselves into four groups. Group I consists of six cores with slopes ranging from 0·26 to 0·57, with an average of 0·44. Group II contains five

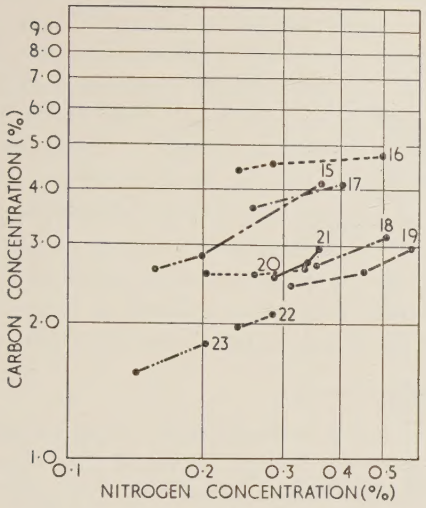

Fig. 3. Logarithmic carbon-nitrogen relations in sediment cores taken from a Maine fjord. The points indicated by the core number are the surface samples. Each subsequent point is a successive subsurface sample with samples from each core joined by a line.

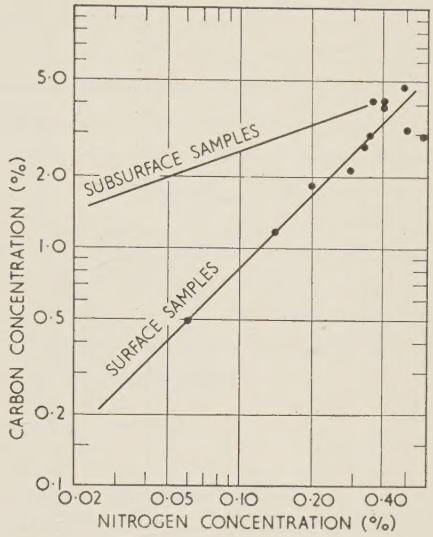

Fig. 4. Comparison of logarithmic carbon and nitrogen relations for surface and subsurface samples from a Maine fjord. The subsurface line is derived from the mean slope of the nine cores.

cores, the slopes of which range from 0·78 to 1·07, with a mean value of 0·89. Group III consists of five cores ranging in slope from 1·37 to 1·60; the average is 1·45. The two cores in Group IV have very steep slopes of 7·11 and 57·29; the average slope as calculated from their angles is 14·00. Unfortunately, size analysis data for all samples are not available for comparison.

Waksman (1933) obtained two cores from the Gulf of Maine which show with increasing depth relatively uniform particle sizes and also a steady decrease in organic matter. A third core acquires these characteristics at a subsurface level of about 35 cm. Both of these factors, present also in the nine Gulf of Maine cores used in this study, indicate a relatively stable depositional environment. The slopes of the lines representing the logarithmic relation of carbon and nitrogen for these cores is 0·14, 0·27, and 0·93. The mean value is 0·44. Waksman also presented information on the carbon and nitrogen for a single core from the vicinity of Spitzbergen. The average slope of the carbon-nitrogen line is 0·75.

Emery and Rittenberg (1952) presented some information on the carbon and nitrogen content of subsurface samples from the Channel Islands region of California. From their data it was found that the slopes of the carbon-nitrogen lines of each core fell into two groups. Group I consists of four cores with slopes ranging from 0·46 to 0·62, with an average of 0·55. Group II is composed of six cores with slopes

ranging from 0·87 to 1·96, for an average of 1·19. Marked indications of environmental changes with time are in evidence in these samples, since both particle size and organic content have appreciable vertical changes.

Arrhenius (1952) shows that for clays in the North Equatorial Pacific, the

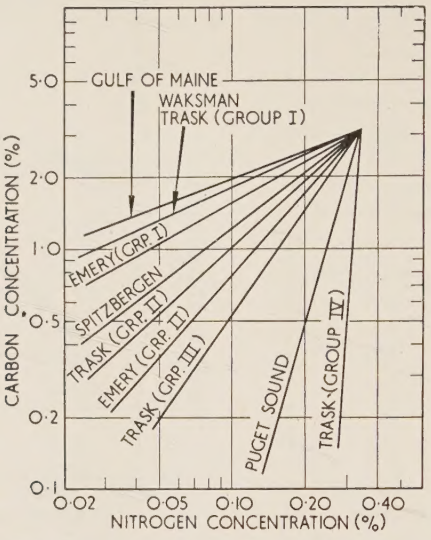

Fig. 5. Comparison of subsurface carbon and nitrogen data from various sources. The point of origin represents the average surface carbon and nitrogen content of all core samples considered.

carbon-nitrogen ratio decreases downward, carbon being lost more rapidly than nitrogen. Under these conditions the resultant slope of any statistical logarithmic line must be greater than 1.

Conclusions

(1) From the available data obtained from various regions, the association of carbon and nitrogen exhibits wide differences. The C/N ratio may have a direct or indirect relation with both increasing of decreasing organic material.

(2) The slopes of the statistical lines, representing an approximate logarithmic function, show quite a different relationship between the carbon and nitrogen for surface and subsurface samples in a single area (Fig. 4). This can be attributed to environmental control. Surface samples are intimately associated with both supply and decomposition of the organic material. The subsurface sediments are essentially isolated from continuous organic supply; decomposition is the primary active factor. Anaerobic conditions exist both on and below the surface of the fjord sediments, thus other factors, possibly of a biochemical and microbiological nature, may control the ratio of carbon to nitrogen loss.

(3) When considering the C/N ratio of subsurface samples, one might logically conclude that the ratio should increase with increasing depth. This would be based on the relative ease of nitrogen mobility over carbon mobility. From the spectrum of lines representing the carbon-nitrogen relationship of subsurface sediments from various areas as shown in Fig. 5, it is apparent however that the general subsurface

anaerobic environment may produce both increasing or decreasing C/N ratios with increasing depth. This may be due to local environmental conditions as controlled by the type and amount of bacteriological decomposition and/or to quantitative and qualitative differences in the organic supply. In turn the bacteriological effect is also a function of dissolved inorganic constituents, mineralogical composition, and certain physical characteristics of the sediments.

(4) Though the depositional and post-depositional environment of organic decomposition are of primary importance in regulating the C/N ratio, the type of organic material supplied to the sediments must also be seriously considered. A sediment receiving a high proportion of lignin has the possibility of developing an abundance of ligno-protein complexes via bacterial activity. These nitrogen-bearing complexes are extremely resistant to decay, and their formation, as controlled in part by the organic supply, may well be associated with the relation between carbon and nitrogen, particularly evident in subsurface sediments.

(5) General conclusions as to the type of relationship between carbon and nitrogen in both surface and subsurface marine sediments from scattered areas cannot be drawn. Each area must be evaluated as a single entity.

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The occurrence of magnesian calcites in nature

JULIAN R. GOLDSMITH,* DONALD L. GRAF,† and OIVA I. JOENSUU*

(*Received* 10 *January* 1955)

ABSTRACT

Diagrams correlating X-ray spacing and Mg substitution in calcite, based upon spectrochemical analysis and powder diffraction data, are presented for several X-ray reflections. The Mg content of natural magnesian calcites is correlated with the P_{CO_2}, T relations in the system CaO—MgO—CO_2. Sedimentary and other low-temperature calcites are shown to be very low in Mg, with the exception of certain metastable materials. Metamorphic carbonates commonly contain dolomite associated with calcite containing significant amounts of $MgCO_3$ in solid solution. $MgCO_3$ contents up to ~9 mol per cent have been observed in granulite-facies rocks and in predazzite from the Tyrol, corresponding to a minimum equilibrium temperature of ~600°C. Blebs of dolomite within single calcite grains of some metamorphic carbonates are believed to be exsolution textures, on the basis of optical and X-ray examination.

Low Mg contents of calcites that may once have been at high temperatures may be a consequence of such factors as: (1) exsolution during cooling; (2) CO_2 pressures insufficient to maintain significant Mg in solid solution; (3) postmetamorphic retrograde processes, including low-temperature hydrothermal action and weathering; and (4) an environment poor in Mg.

INTRODUCTION

CLARKE and WHEELER (1922) reported sizable amounts of Mg in their chemical analyses of the skeletal material of certain marine invertebrates. FOOTE and BRADLEY (1914), FORD (1917), and BILIBIN (1927) assumed that the Mg found in the analyses of calcites, apparently single crystals, was in solid solution. Not until the recent work of CHAVE (1952, 1954a, 1954b)‡ and SPOTTS (1952), however, was an actual correlation made between chemical analyses and X-ray diffraction, clearly indicating that the calcite structure can accommodate a considerable amount of Mg in solid solution. The preceding paper (GRAF and GOLDSMITH, 1955) discusses the equilibrium relations between Mg content, temperature, and CO_2 pressure. CHAVE and SPOTTS were concerned with the skeletal parts of marine organisms, and with limestones containing such material. The present investigation is concerned with the magnesian calcites from a somewhat wider variety of occurrences, both organic and inorganic.

CHAVE (1952) published a curve correlating Mg content with the d value of the strongest X-ray reflection. Several such curves, independently determined by us for several different X-ray reflections, are presented here. These curves are then used for establishing the composition, from X-ray data, of a wider variety of magnesian calcites. These data are used only to obtain an estimate of the upper limits of Mg substitution in the calcites of various environments; detailed studies of individual occurrences are needed.

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‡ CHAVE's use of the expression "solid solution between calcite and dolomite" is misleading; compositionally, this expression is permissible, but structurally it fails to take into account the ordered nature of dolomite, and the fact that this ordering does not exist when there is significant deviation from a 1 : 1 Ca : Mg ratio. It should also be noted that CHAVE's "$d_{(100)}$," based on the cleavage rhombohedron, should be $d_{(200)}$, which is equivalent to $d_{(112)}$ of the true rhombohedral unit cell as used in this paper.

Experimental Techniques

Spectrochemical method

A Jaco-Wadsworth 21-foot grating spectrograph (Jarrell-Ash Co.) was used. The sample electrodes were made from 1/8-inch rods of National Carbon Co. grade L-113SP Special Carbon Spectroscopic Electrodes by drilling 1/16-inch holes to a depth of 4 mm. The counter electrode was a piece of the rod pointed with a pencil sharpener. A 220-volt d.c. power source was used, the current adjusted to 5 amperes when the electrodes were closed. The sample electrode was made positive, and the arc gap kept at 4 mm during the exposure. A rotating sector with the step ratio 1 : 2, giving six steps, was placed in front of the slit, which was set at 0·04 mm. Kodak SA No. 1 plates were used for the ultraviolet part of the spectrum, Kodak IV-F plates for the visible portion. The plates were developed in Kodak D-19 for three minutes at 21°C. The photometric measurements were made with a Jaco densitometer (Jarrell-Ash Co.) and the plates were calibrated with stepped sample spectra. The Seidel transformation, $\Delta = \log (100/\%T - 1)$ (where 100 is the percent transmittance from the clear portion of the plate and T the transmittance from the line), was plotted against the log step ratio. This procedure gives a calibration curve that is close to a straight line for the SA No. 1 and IV-F emulsions (Hohnerjäger-Sohm and Kaiser). The log intensity ratios are computed with a calibration board, as described by these authors. In the working curve, the concentration is plotted against the log intensity ratio of the analysis line to the internal standard line.

The standards were made by mixing strontium carbonate and oxides of aluminium, iron, magnesium, manganese, and silicon with Iceland spar.

Direct arcing of calcite and dolomite was attempted, but some difficulty with evolved CO_2 blowing the sample out of the electrode was encountered. Therefore, all samples were fused prior to arcing (Hasler and Barley, 1952). An internal standard was prepared by thoroughly mixing 5 per cent cobalt oxide and 20 per cent barium carbonate with 75 per cent lithium carbonate. One part of the mixture and one part of the sample were weighed into an agate mortar. Two parts of lithium carbonate and four parts of crystalline boric acid were added and mixed. The samples were weighed with a torsion balance (Roller Smith Co.) having a precision of 0·02 mg. The mixed sample was transferred to a graphite crucible and fused at 900°C for twenty minutes, and the resulting borate bead crushed and mixed with an equal amount of graphite powder. Two electrodes were filled and arced.

The spectrum lines used for analysis are as follows:

Element	*Wavelength*, Å	*Concentration range, wt. per cent*	*Internal standard*
Ca	2,997·3	10–60	Ba 3071·5
Ca	3,006·8	10–60	Ba 3071·5
Mg	2,782·9	1–15	Co 2648·6
Mg	2,779·8	0·1–2	Co 2648·6
Mg	3,336·6	10–50	Co 3334·1
Al	3,082·1	0·1–1	Co 3072·3
Al	2,660·3	0·3–20	Co 2648·6
Fe	3,067·2	1–20	Co 3072·3
Fe	3,020·6	0·05–1	Co 3072·3
Si	2,987·6	5–100	Co 3072·3
Si	2,881·5	0·05–5	Co 3072·3
Mn	2,801·0	0·005–0·3	Co 3072·3
Mn	2,949·2	0·2–3	Co 3072·3
Sr	4,607·3	0·05–1	Ba 4523·2

The precision of the method is ±5 per cent of the amount present, or better, for all of the analyzed elements. As a check, five samples of the Bureau of Standards Limestone No. 1a and Dolomite No. 88 were fused and analyzed, with the following results:

	Limestone		*Dolomite*	
	Chemical	*Spectrographic*	*Chemical*	*Spectrographic*
SiO_2	14·11	14·2, 14·5, 14·7, 13·7	0·31	0·4, 0·35, 0·35, 0·35
Fe	1·14	1·05, 1·05, 1·15, 1·10	0·059	0·050, 0·055, 0·057, 0·050
Al_2O_3	4·16	4·1, 4·15, 4·25, 4·2	0·067	
TiO_2	0·16	0·16, 0·15, 0·15, 0·15	0·005	
MnO	0·038	0·050, 0·045, 0·050, 0·051	0·006	Less than 0·01
CaO	41·32	40·5, 40·7, 41·0, 41·0	30·49	30·7, 30·5, 31·0, 30·0
SrO	0·12		< 0·01	
MgO	2·19	2·1, 2·1, 2·0, 2·15	21·48	22·0, 21·5, 21·3, 21·7

X-ray diffraction

The X-ray analyses of the powdered specimens were carried out with North American Philips 114·59 mm cameras using filtered Fe radiation, and with a Nonius quadruple-focusing camera using Co radiation monochromatized with a bent quartz crystal.

A correction for film shrinkage of patterns taken with the Philips camera was made by making use of the Straumanis-type mount; measurement of the actual distance between centres through the use of both front and back reflections is readily accomplished. Measurements of reflections were converted to spacing values and subtracted from the values obtained from measurements on Johnson-Mathey's Specpure $CaCO_3$, to obtain Δd values. Four samples are simultaneously irradiated in the Nonius camera, and four diffraction patterns are obtained on the same film. By always using the Specpure $CaCO_3$ as a standard in one of the four positions, errors due to film shrinkage and departure from ideal camera dimensions are compensated for and $\Delta d = (d_{(\text{standard})} - d_{(\text{sample})})$ is directly obtained.

The strongest reflection of calcite, dolomite, and magnesite is (112), referred to the true rhombohedral unit cell (BRADLEY, BURST, and GRAF, 1953). The observed shift of this reflection with changing Mg-content was useful for compositional determination, particularly for carbonate phases of such dilution in the total sample that the weaker reflections were not measurable. The (112) reflection is of fairly low θ angle (d = 3·036 Å for pure calcite, 2·89 Å for dolomite), and therefore the Nonius camera with an effective Debye diameter of 229 mm was used for measurement of this reflection, using Co radiation.

Whenever a sufficient amount of a well-crystallized carbonate phase was present so that back reflections were measurable, several reflections of high θ value were measured on films taken with the Philips camera, using Fe radiation. The change in spacing of two $K\alpha_1$ reflections was used for compositional determination. The measured spacings of these reflections for Specpure calcite were d = 1·0451 Å and 1·0119 Å. The spacings of all reflections of calcite up to $(h^2 + k^2 + l^2) = 100$ were calculated, using the lattice constant $d_{(112)}$ = 3·0357 Å (BIRGE, 1941) and $\alpha_{(\text{cleavage rhombohedron})} = 101^\circ\ 54'\ 3''$ (average of values of TU, BEARDEN, and IEVENS and STRAUMANIS, cited in IEVENS and STRAUMANIS, 1940). Calculated spacings in the region of those observed for the two back reflections are:

Index	*Calculated spacing*, Å
(644)	1·0615
(400)	1·0473
(521)	1·0449
(531)	1·0421
(655)	1·0353
(654)	1·0350
(643)	1·0231
(633) (552)	1·0119
($\bar{3}20$) ($3\bar{2}0$)	0·9898
($3\bar{2}1$)	0·9847

The two back reflections used thus appear to be (521) and (633), (552). Some measurements were also made of the spacing change with composition of the (444) and (11$\bar{2}$) reflections (d = 1·4218 and 1·4405 Å, respectively, for pure calcite), using the Philips camera. These reflections are a measure of the c and a axes, respectively, in the hexagonal unit cell.

Relation Between Magnesium Content and X-ray Spacings of Calcite

A suite of calcite specimens of various Mg contents was assembled for X-ray and analytical work. The specimens consisted of single-phase carbonate material as

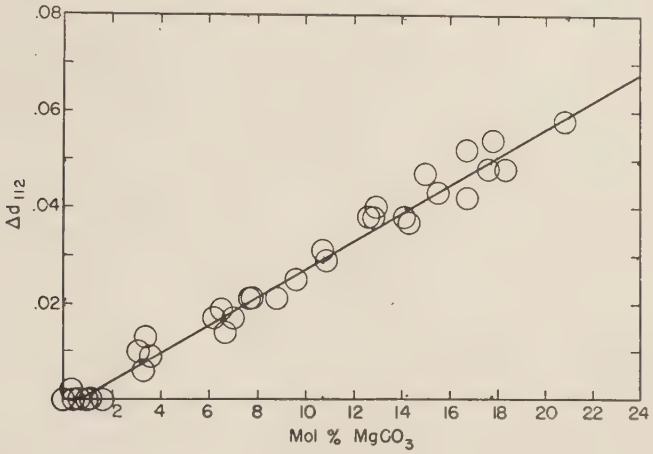

Fig. 1. Variation of (112) spacing of natural calcites with increasing substitution of Mg, referred to Specpure $CaCO_3$ as standard (see Table 1). The straight line was obtained by least-squares analysis.

determined by the absence of extraneous X-ray reflections, or of assemblages from which single-phase carbonate could be segregated. Most of the specimens suitable for this purpose and containing a reasonably high Mg content are skeletal remains of present-day marine organisms. The high concentration of Mg in these organisms is metastable under earth-surface conditions (Graf and Goldsmith, 1955).

Table 1 lists the specimens in order of increasing mol per cent $MgCO_3$, as determined spectrographically. Also included in Table 1 are the $\Delta d_{(112)}$ values. These data are presented in Fig. 1 as a straight line plot of $\Delta d_{(112)}$ versus mol per cent $MgCO_3$.

Figs. 2 and 3 are plots of $\Delta d_{(521)}$ and $\Delta d_{(663),\ (552)}$ vs. mol per cent $MgCO_3$, based upon measurements made from Philips patterns of those substances in Table 1 which give back reflections of suitable quality. Similarly, Figs. 4 and 5 present the data for $\Delta d_{(11\bar{2})}$ and $\Delta d_{(444)}$. All are drawn as straight lines.

We obtained $\Delta d_{(112)}$ values for pure synthetic magnesite and for the dolomite from Serra das Eguas, Brazil. These values, obtained using Specpure calcite as a standard, are:

$$\text{Dolomite, } \Delta d_{(112)} = 0{\cdot}146 \text{ Å}$$

$$\text{Magnesite, } \Delta d_{(112)} = 0{\cdot}291 \text{ Å}$$

The same value for dolomite is obtained by subtracting $d_{(112)}$ of dolomite = 2·89 Å (Schoklitsch, 1935, for a dolomite in which Fe : Mg = 1 : 32) from $d_{(112)}$

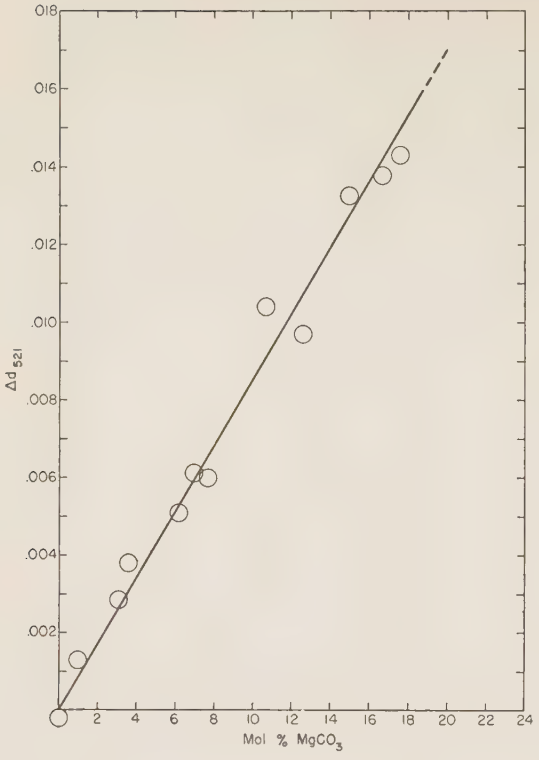

Fig. 2. Variation of (521) spacing of natural calcites with increasing substitution of Mg, referred to Specpure $CaCO_3$ as standard.

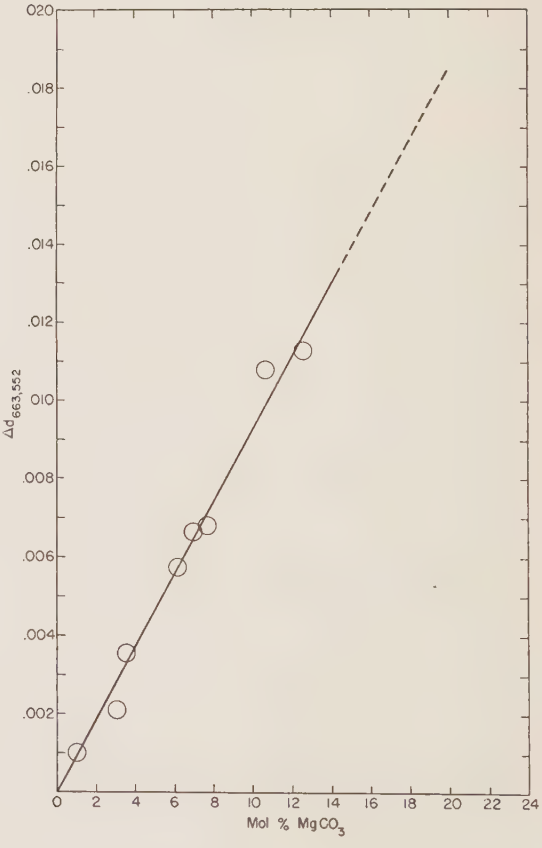

Fig. 3. Variation in spacing of (663), (552) reflection for natural calcites with increasing substitution of Mg, referred to Specpure $CaCO_3$ as standard.

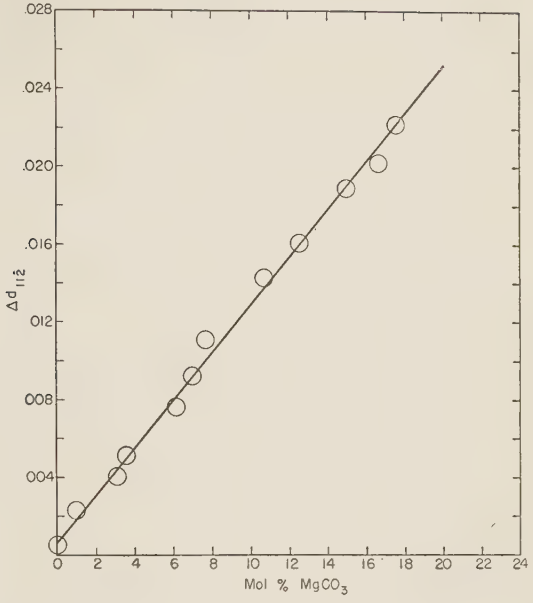

Fig. 4. Variation of $(11\bar{2})$ spacing of natural calcites with increasing substitution of Mg, referred to Specpure $CaCO_3$ as standard.

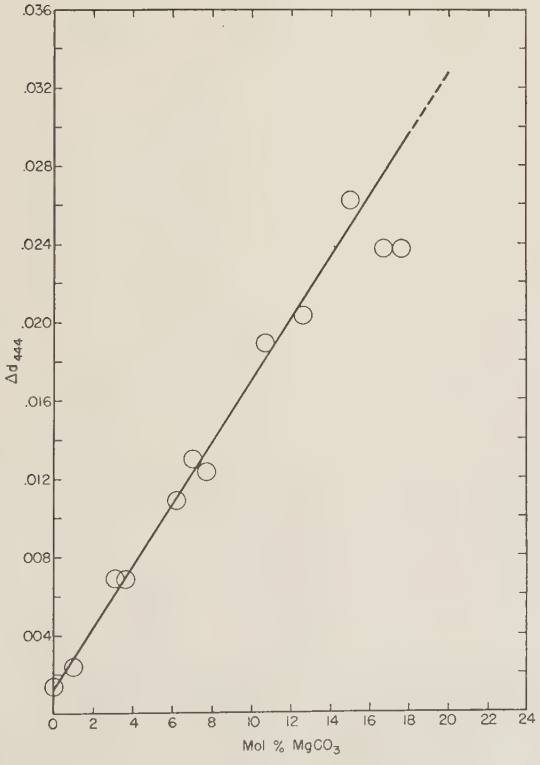

Fig. 5. Variation of (444) spacing of natural calcites with increasing substitution of Mg, referred to Specpure $CaCO_3$ as standard.

Table 1

Spectrographic analyses of naturally occurring calcites, recalculated to 100 per cent Ca and Mg carbonates. The final column gives the difference in spacing between (112) of Specpure calcite and that of each of these materials. Percentages are in weight percent except for the next to the last column.

No.	*Description*	Fe	Al_2O_3	SiO_2	MnO	MgO	CaO	SrO	$CaCO_3$	$MgCO_3$	$SrCO_3$	$\frac{CaCO_3}{+MgCO_3}$	*Wt.* % $\frac{MgCO_3}{CaCO_3 + MgCO_3} \times 100$	*Mol.* % $MgCO_3$	$\Delta d_{(112,\ \text{Nonius})}$
1	Calcite, Cordoba, Argentina	tr.	—	—	tr.	< 0·1	55	< 0·1	98	< 0·2	—	98	< 0·2	< 0·2	0·000
2	Calcite, Hybla, Ontario	0·09	—	—	0·090	0·15	54	0·13	96·5	0·3	0·17	96·8	0·3	0·3	0·000
3	Calcite, Guanajuato, Mexico	0·06	—	—	0·065	0·15	57	0·10	102	0·3	0·14	102·3	0·3	0·3	0·002
4	Calcite, Oklahoma	tr.	—	—	tr.	0·3	55	< 0·1	98	0·6	—	98·6	0·6	0·7	0·000
5	Calcite, loc. unknown	0·085	—	—	0·085	0·45	55	< 0·1	98	0·9	—	98·9	0·9	1·0	0·000
6	Oyster	tr.	—	—	tr.	0·5	56	0·09	100	1·0	0·12	101	1·0	1·1	0·000
7	Barnacle, Japan	tr.	—	—	tr.	0·8	57	0·28	102	1·7	0·37	103·7	1·6	1·8	0·000
8	Echnoid spines, *Strongylocentrotus purpuratus*, California	tr.	—	—	tr.	1·3	52·5	0·16	94	2·7	0·21	96·7	2·8	3·1	0·010
9	Echnoid spines, *Strongylocentrotus purpuratus*, Corona del Mar, California	tr.	—	—	tr.	1·45	56	0·20	98	3·0	0·28	101	3·0	3·3	0·006
10	Marble, Essex Co., N.Y.	0·88	—	—	0·05	1·5	55	0·09	98	3·1	0·12	101·1	3·1	3·4	0·013
11	Marble, granulite facies, Greenland	0·1	—	—	0·04	1·45	50	< 0·1	89	3·0	—	92	3·3	3·6	0·009
12	Echnoid spines, Florida	tr.	—	—	tr.	2·5	49·5	0·16	88·5	5·2	0·21	93·7	5·6	6·2	0·017
13	Echnoid spines	tr.	—	—	tr.	2·7	50	0·25	89	5·6	0·33	94·6	5·9	6·5	0·019
14	Test of 9	tr.	—	—	tr.	2·9	52·5	0·17	94	6·1	0·23	100·1	6·1	6·7	0·014
15	Echnoid test	tr.	—	—	tr.	2·9	49·5	0·18	88·5	6·1	0·24	94·6	6·4	7·0	0·017
16	Echnoid test	tr.	—	—	tr.	3·0	47	0·21	84	6·3	0·29	90·3	7·0	7·7	0·021
17	Echnoid test, *Strongylocentrotus purpuratus*, Calif.	tr.	—	—	tr.	3·4	52	0·21	93	7·1	0·29	100·1	7·1	7·8	0·021
18	Echnoid test	tr.	—	—	tr.	3·7	50	0·18	89	7·7	0·24	96·7	8·0	8·8	0·021
19	Echnoid test	tr.	—	—	tr.	3·8	47	0·20	84	8·0	0·28	92	8·7	9·6	0·025
20	Echnoid test, Saipan	tr.	—	—	tr.	4·6	50	0·18	89	9·6	0·24	98·6	9·7	10·7	0·031
21	Echnoid test	tr.	—	—	tr.	4·7	50	0·20	89	9·8	0·28	98·8	9·9	10·9	0·029
22	Echnoid test, Saipan	tr.	—	—	tr.	5·5	50	0·19	89	11·5	0·25	100·5	11·5	12·6	0·038
23	*Piaster ochraceus*	tr.	—	—	tr.	5·6	50	0·18	89	11·7	0·24	100·7	11·6	12·8	0·038
24	Calc. algae, *Corallina* sp., California	tr.	0·75	~1	tr.	5·0	44	0·18	78·5	10·5	0·24	89	11·7	12·9	0·040
25	Foraminifera, Bermuda	tr.	—	—	tr.	5·9	47	0·19	84	12·3	0·25	96·3	12·8	14·1	0·038
26	Calc. algae, *Bossea* sp., California	0·35	2·4	12·5	tr.	4·9	38	0·13	68	10·2	0·17	78·2	13·0	14·3	0·037
27	Calc. algae, *Lithothamnium* sp., Bermuda	tr.	—	—	tr.	6·5	48	0·18	86	13·6	0·24	99·6	13·6	15·0	0·047
28	Calc. algae, *Lithothamnium* sp., California	1·6	2·5	17·5	0·04	5·5	39	0·13	70	11·5	0·17	81·5	14·1	15·5	0·043
29	Calc. algae, *Bossea* sp., California	0·05	0·5	4·0	tr.	6·0	39	0·16	70	12·5	0·21	82·5	15·2	16·7	0·042
30	Calc. algae, *Lithophyllum* sp., West Boiler, Bermuda	tr.	—	—	tr.	6·4	42	0·27	75	13·4	0·36	88·4	15·2	16·7	0·052
31	Calc. algae, *Lithophyllum* sp., Palau	tr.	—	—	tr.	7·3	45	0·21	80·5	15·3	0·29	95·8	16·0	17·6	0·048
32	Calc. algae, *Lithophyllum* sp., Palau	tr.	—	—	tr.	7·6	46	0·23	82	15·9	0·30	97·9	16·2	17·8	0·054
33	Calc. algae, Bermuda	tr.	—	—	tr.	7·6	45	0·20	80	15·9	0·27	95·9	16·6	18·3	0·048
34	Calc. algae, *Goniolithon* sp., Florida	tr.	—	—	tr.	7·8	39	0·24	70	16·3	0·32	86·3	18·9	20·8	0·058

of calcite = 3·0357 Å (Birge, 1941). These data are plotted in Fig. 6 along with the curve of Fig. 1, extrapolated all the way to magnesite. The extrapolated curve passes very close to the plotted value for dolomite, and through the plotted point for magnesite. This rather remarkable agreement between extrapolated and

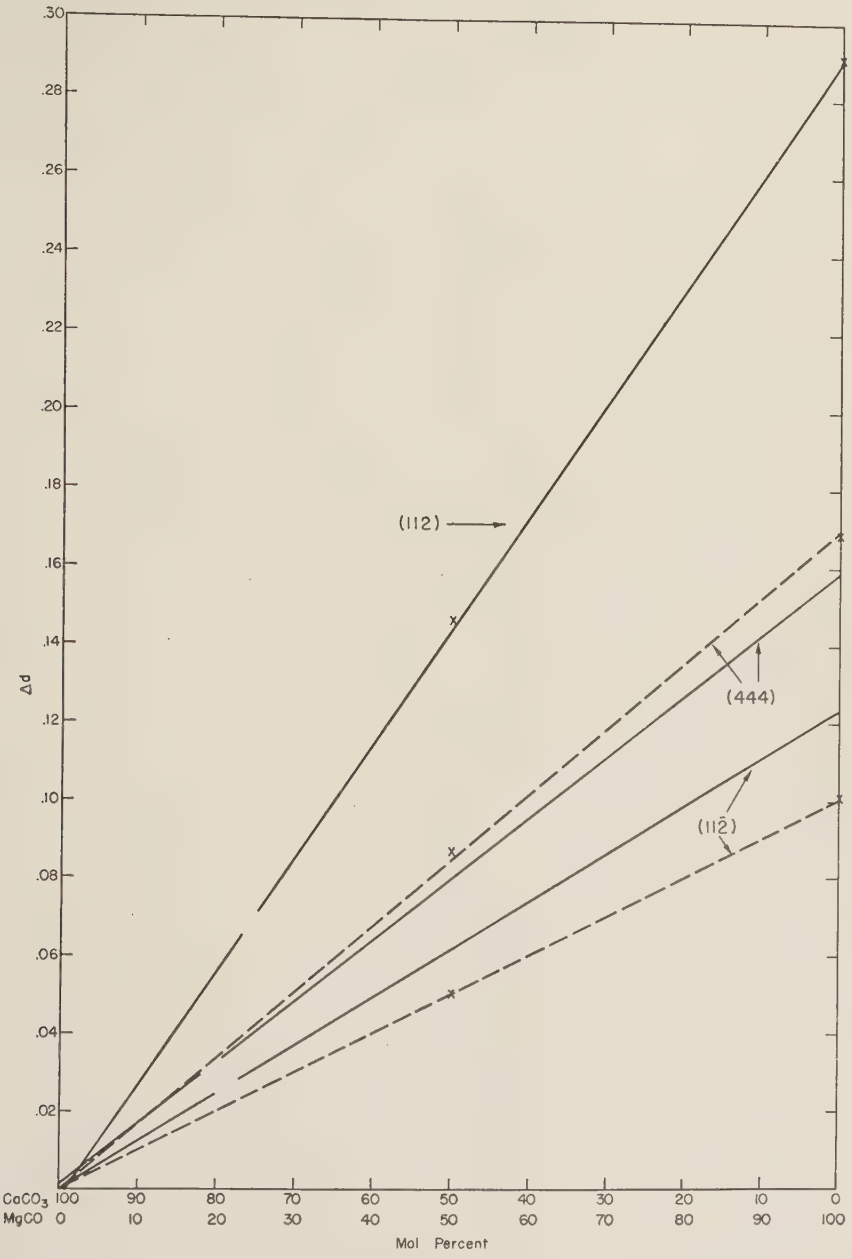

Fig. 6. Extrapolation of the data of Figs. 1, 4, and 5, for comparison with measured spacings of dolomite and magnesite.

measured values is surely in part fortuitous, especially considering the expanded scale upon which the data are plotted.

Fig. 6 also contains our measured values of $\Delta d_{(11\bar{2})}$ and $\Delta d_{(444)}$ for dolomite and magnesite. The dashed lines represent the best fit of a straight line from calcite through dolomite to magnesite, and indicate that the a and c axis spacings of these three substances also lie on a straight line, within the limit of error of measurement. However, the extrapolated straight line curves of Figs. 4 and 5 deviate considerably from the "ideal" dashed lines. In view of the uncertainty of the compositional data on which Figs. 4 and 5 are based, it is not possible at present to state with assurance that the indicated nonuniform a-axis : c-axis contraction is real; further work is in progress. The possibility of deviation of the curves from straight lines must also be kept in mind. It should be noted that the observed projection of the (112) data for disordered magnesian calcites, through the (112) value for (ordered) dolomite, may be a fortuitous consequence of the inclination of this plane to both a and c.

Discussion of the Compositional Data and of Several Possible Errors Involved

Table 2 presents wet chemical analyses of five of the specimens listed in Table 1. Spectrographic determinations of mol per cent $MgCO_3$ are included for comparison. In all cases the wet chemical values for $MgCO_3$ are higher than the spectrographic values. Nos. 9, 14, and 15 are close to the combined experimental error of the two analytical methods, but Nos. 24 and 31 are clearly outside of this limit. This discrepancy cannot be explained on the basis of the evidence on hand.

Chave's (1952) curve is shown as a straight line up to ~17 wt. per cent (~18·7 mol per cent) $MgCO_3$, at which point it rapidly tails off as though additional Mg had little effect on the calcite cell size. This appears rather unlikely from crystal chemical considerations, and would suggest either an analytical error at higher Mg concentrations, or the presence of Mg in phases other than calcite. We have not observed any algal calcites with Mg content as high as those listed by Chave, but have observed the presence of Mg, in algal materials, in concentrations greater than those evidenced from the X-ray spacings. This was discovered when several of the algal calcites were heated at elevated temperatures and CO_2 pressures (Graf and Goldsmith, 1955), in the P,T range where approximately 25 mol per cent $MgCO_3$ would be stable in the calcite structure. X-ray spacings indicative of $MgCO_3$ contents of ~21 mol per cent were observed in algal calcites that showed ~19 mol per cent before thermal treatment. It is apparent that finely divided or adsorbed Mg exists in some form other than in the calcite structure in at least some of the algal materials. The writers were somewhat surprised that the extraneous Mg did not produce a tailing off in the various compositions vs. X-ray spacing curves, inasmuch as the calcites with the higher Mg contents were principally algal materials.

The analyses of Table 1 were recalculated to 100 per cent Ca and Mg carbonate. Several of the samples contained sizable amounts of noncarbonate materials which did not interfere with the X-ray measurements and were assumed not to contain significant amounts of Ca or Mg. A correction for the effect of solid solution of Fe

and Mn upon the X-ray spacings of these samples is in most cases so small that it falls within the experimental limit of error. The Fe contained in the highly impure sample No. 28 is probably not present in the calcite, and a correction thus seems unnecessary. It is likely that the Fe in the colourless single-phase calcite of sample No. 10 is in solid solution, and correcting accordingly would move that point closer

Table 2

Comparison of $MgCO_3$ contents obtained by wet-chemical and spectrographic analyses. See Table 1 for the complete spectrographic analyses.

	Echnoid spines *Strongylocentrotus purpuratus*, Corona del Mar, Calif. No. 9*	Echnoid test *Strongylocentrotus purpuratus*, Corona del Mar, Calif. No. 14*	Calcareous algae, *Corallina* sp., California No. 24*	Echnoid test No. 15†	Calcareous algae, *Lithophyllum* sp., Paulau No. 31†
SiO_2	—	—	—	—	0·10
R_2O_3 excl. Fe_2O_3	—	—	—	—	0·19
Fe	0·03	0·01	0·22	(< 0·02)	0·01
Mn	0·00	0·00	0·01	0·003	—
CaO	52·33	50·22	42·45	49·99	42·83
MgO	1·55	3·06	5·74	2·98	8·40
CO_2	42·36	42·06	38·42	41·68	41·48
H_2O + org. material	2·64	3·35	5·71	—	—
Organic C	—	—	—	0·65	—
Total H as H_2O (> 110°F)	—	—	—	3·01	—
H_2O < 110°F	—	—	—	0·22	—
Insol.	0·02	0·00	7·18	—	—
Total	98·93	98·70	99·73	98·53	93·01
Wt. % $MgCO_3$ = $\frac{MgCO_3}{CaCO_3 + MgCO_3} \times 100$	3·4	6·7	13·8	6·6	18·9
Mol % $MgCO_3$	3·7	7·4	15·2	7·3	20·8
Mol % $MgCO_3$ (Spectr.)	3·3	6·7	12·9	7·0	17·6

* Analyst: H. B. Wiik.
† Analyst: L. D. McVicker.

to the curve. Even so, changing one or two of the points would have no effect on the curve as a whole. The samples in Table 1 contain as much 0·37 wt. per cent $SrCO_3$. If one assumes the change in the calcite cell to be directly proportional to the difference in ionic radius between Ca and whatever cation is substituted for it, then it can be shown that 0·37 wt. per cent $SrCO_3$ would have an effect equal and opposite to that of ~0·13 wt. per cent $MgCO_3$. This is well within the overall experimental error, and no correction for Sr in these reference specimens is necessary.

Examination of Natural Magnesian Calcites

Once the curves for X-ray spacings vs. Mg substitution were established, a considerable number of natural carbonates from different geologic environments were examined by X-ray powder diffraction. The Mg contents of these specimens, assuming all variation in X-ray spacing to be due to Mg, are listed in Tables 3 and 4. The Mg contents determined from the pictures taken with the Philips camera represent averages of the values obtained from the (521) and (663), (552) reflections.

Table 3

Low-temperature magnesian calcites.

Number	*Description*	*Mol* % $MgCO_3$*
35	Dendritic tufa, Mono Lake, California	2·6
36	Thinolitic tufa, Mono Lake, California	3·3†
37	Lithoid tufa, Mono Lake, California	0·7
38	Tufa deposited around algae, fresh-water lake, Michigan	2·0
39	Dolomitic Pleistocene marl, Florida	3·5
40	Avon Park limestone (Middle Eocene), containing a little dolomite, and clay and organic matter	0·6
41	Powdery calcite, Currant Creek magnesite deposit, Nevada	2·6
42	Powdery calcite, Currant Creek magnesite deposit, Nevada	4·7
43	Powdery calcite and dolomite with deweylite, Currant Creek magnesite deposit, Nevada	7·5†
44	Calcareous tufa, Yellowstone National Park, Wyoming	1·8

* Assuming all spacing change to be due to $MgCO_3$.
† Analyzed spectrographically, see Table 5.

Substitution of Mn and/or Fe in the calcite structure would produce a spacing change in the same direction as that produced by Mg. Conditions that would permit the incorporation of Mg in the calcite structure might also be assumed favourable to the admission of Fe and Mn, if these elements were available. To get some insight into the magnitude of this effect in the samples of Tables 3 and 4, spectrographic analyses were made of a number of samples from different environments which showed rather large spacing changes. These analyses are assembled in Table 5 and give an approximate figure for the upper limit of Mg substitution observed in the calcites of several natural environments. Inasmuch as these analyses were made to evaluate Fe and Mn contents, no attempt was made to separate out dolomite, and therefore the Mg contents are not representative of the calcite phase alone.

Only in sample No. 75 is the sum of Fe and Mn high enough to break down the general assumption that the observed spacing changes in calcite are due to Mg substitution. In this sample as much as half of the "6·4 mol per cent $MgCO_3$" may actually be $FeCO_3$ and $MnCO_3$ in solid solution. In several other samples, such as Nos. 48 and 61, the sum of Fe and Mn is sufficient that a correction of the "$MgCO_3$ content" may be justified. However, it may well be that Fe and Mn are

Table 4

Mg content of selected natural calcites, based upon the assumption that deviation of X-ray spacings from those of the standard, Specpure $CaCO_3$, is due entirely to substitution of Mg. The mineralogical assemblages given above are each based upon the results of a single X-ray powder diagram of a small portion of the specimen, which may not be representative. In particular, dolomite may be present in some specimens for which it is not listed.

Number	*Description*	*Mol %* $MgCO_3$
	Carbonate beds in granulite facies rocks, West Greenland	
45	Calcite-dolomite marble	4·1
46	Calcite marble	2·2
47	Calcite-dolomite marble	7·9†
48	Calcite-dolomite marble	8·6†
49	Calcite-bearing diopside skarn	2·9
50	Dolomite marble, containing a little calcite	8·6
51	Calcite marble, containing a little dolomite	3·5, 8·6*
52	Calcite marble, containing a little dolomite	1·3, 7·9*†
53	Calcite marble	4·9
54	Calcite marble	6·6
55	Calcite-dolomite marble	7·1
56	Calcite marble, containing a little dolomite	2·9
57	Salmon-coloured calcite marble	3·6
58	Phlogopite-calcite marble	6·6
59	Calcite marble	2·6
60	Calcite marble	6·6
61	Calcite-dolomite marble	3·5, 7·9*†
62	Calcite-dolomite marble	5·7
63	Calcite-dolomite marble	4·4
	Carbonate beds surrounded and replaced by hornblende syenite, Laramie Range, Wyoming	
64	Calcite-dolomite marble	3·2†
65	Calcite-dolomite marble	4·0
66	Calcite marble	1·8
	Adirondack area, New York	
67	Calcite-dolomite-graphite-silicate marble	2·0, 4·8*
68	Calcite marble	3·2
69	Calcite-dolomite-graphite-silicate marble	1·8, 4·6*
70	Calcite-phlogopite-diopside marble	6·6
71	Calcite-dolomite-phlogopite-graphite marble	5·1
72	Calcite-dolomite-graphite-silicate marble	4·4
73	Calcite veinlet cutting dolomite	2·2
74	Calcite-dolomite marble, amphibolite facies, Gouveneur, N.Y.	6·0†
75	Silicated calcite marble, amphibolite facies, Balmat, N.Y.	6·4†
76	Calcite-dolomite marble, amphibolite facies, Black Lake, N.Y.	3·4
77	Calcite marble, amphibolite facies, Black Lake, N.Y.	5·1†
78	Dolomite marble containing some calcite	1·5
79	Calcite-bearing skarn, granulite facies, Clifton, N.Y.	2·0
80	Calcite-dolomite marble, greenschist facies, Sierra Pelona, California	2·6
81	Yule marble, Colorado	0·6
	Hunza State, Pakistan	
82	Unweathered grey calcite marble	3·0†
83	Calcite-dolomite-phlogopite-graphite-magnetite-garnet marble	5·4†
84	Calcite marble	1·6
	Barstow, California	
85	Calcite-dolomite marble	2·4
86	Calcite-dolomite marble	3·4
87	Calcite-dolomite marble	2·8
	Inwood marble, New York	
88	Calcite marble	2·0
89	Calcite-dolomite marble	4·9†
90	Calcite-dolomite marble	2·7
91	Calcite-dolomite marble	3·2
	Predazzo, Tyrol	
92	Predazzite (calcite, brucite, periclase with a trace of dolomite); figure is for the more Mg-rich of two calcites present	6·8
93	Predazzite (same assemblage as 92)	4·2, 9·2*†
94	Pencatite (calcite, brucite)	3·0
95	Calcite-nepheline rock, Bancroft, Ontario	3·5
96	Pargasite, Pargas, Finland	3·5
97	Calcite marble with a little dolomite, Fen area, Norway	2·3

* Two magnesian calcites present.

† Specimen analyzed spectrographically (see Table 5).

Table 5

Spectrographic analyses of selected natural calcites, made in order to check the effect of Fe and Mn on the observed X-ray spacings. The Mg contents shown above do not represent Mg substitution in the calcite alone, inasmuch as there is admixed dolomite in some of these samples.

Number	*Description*	*Wt. %* Fe	*Wt. %* $FeCO_3$	*Wt. %* Al_2O_3	*Wt. %* SiO_2	*Wt. %* MnO	*Wt. %* $MnCO_3$	*Wt. %* MgO	*Wt. %* CaO	*Mol %* $MgCO_3$ *in Calcite* (*Tables* 3 *and* 4)
43	Powdery calcite and dolomite with deweylite, Currant Creek magnesite deposit, Nevada	0·05	0·10	< 0·1	40·0	< 0·01	< 0·02	29·0	8·3	7·5
36	Thinolitic tufa, Mono Lake, Calif.	0·09	0·187	< 0·1	2·1	< 0·01	< 0·02	2·1	55	3·3
82	Grey calcite marble, unweathered core, Hunza State, Pakistan	< 0·05	< 0·1	< 0·1	0·3	< 0·01	< 0·02	1·1	55·5	3·0
98	Grey calcite marble, reddish weathered surface, Hunza State, Pakistan	< 0·05	< 0·1	< 0·1	< 0·1	< 0·01	< 0·02	0·2	56	~0
83	Calcite-dolomite-phlogopite-graphite-magnetite-garnet marble, Hunza State, Pakistan	< 0·05	< 0·1	< 0·1	< 0·1	< 0·01	< 0·02	3·4	53	5·4
93	Predazzite, Predazzo, Tyrol	< 0·05	< 0·1	< 0·1	0·15	< 0·01	< 0·02	21·5	Ba standard failure	4·2, 9·2
75	Silicated calcite marble, Balmat, N.Y.	0·15	0·31	< 0·1	0·15	1·9	3·08	1·5	52	6·4
77	Calcite marble, Black Lake, N.Y.	< 0·05	< 0·1	< 0·1	1·9	0·018	0·03	1·5	54·5	5·1
74	Calcite-dolomite marble, Gouveneur, N.Y.	0·2	0·41	< 0·1	0·95	0·033	0·05	2·7	53·5	6·0
89	Calcitic-dolomitic Inwood Marble, N.Y.	< 0·05	< 0·1	0·15	1·9	< 0·01	< 0·02	3·35	50	4·9
64	Calcite-dolomite marble, Laramie Range, Wyoming	0·06	0·12	< 0·1	2·3	0·055	0·09	9·6	45·5	3·2
47	Calcite-dolomite marble, West Greenland	0·11	0·23	< 0·1	1·0	0·09	0·15	6·2	50	7·9
61	Calcite marble containing a little dolomite, West Greenland	0·19	0·39	< 0·1	< 0·1	0·20	0·32	3·5	51	3·5, 7·9
52	Calcite marble containing a little dolomite, West Greenland	0·20	0·41	< 0·1	< 0·1	0·06	0·10	2·6	51	1·3, 7·9
48	Calcite-dolomite rock, West Greenland	0·21	0·43	< 0·1	< 0·1	0·17	0·28	5·3	51	8·6

taken into the structure under conditions very similar to those permitting the solid solution of Mg, and therefore conclusions as to the conditions of formation based on spacing changes, to be discussed in the following section, may not be seriously in error if one fails to correct for moderate Fe and Mn contents.

Low-temperature deposits

Calcites crystallized at low temperature in a number of occurrences have X-ray spacings indicative of Mg in solid solution. The highly magnesian calcites produced as hard parts by a variety of marine organisms have been discussed by Chave (1952, 1954a, 1954b), and data on a number of these materials are given in Table 1. Table 3 contains information about several additional low-temperature calcites. Many fairly recent indurated calcareons rocks contain magnesium calcites, but these are commonly examples of agglomerated remains of marine organisms in which Mg has been at least in part retained. Nos. 39 and 40 are probably sediments of this type, and the writers have examined a number of other sedimentary rocks, Eocene to Recent, the calcites of which still retain sizable amounts of Mg. Rocks of this type are described by Chave (1952, 1954b), and Spotts (1952).

Samples 41–44 may have been formed at temperatures above those normally associated with sedimentary processes. The Mg content in the other samples of Table 3, as well as that in the materials formed by marine organisms, is metastable at earth-surface temperatures (Graf and Goldsmith, 1955). Samples 41–44 are included in this category because these magnesian calcites were probably metastable under the moderate temperature conditions at which they were crystallized. Specimens 41–43 are found in a highly magnesian environment, and the calcite appears to be rather variable in Mg content. Poor crystallization and/or a variable Mg content of the powdery material are expressed by the diffuse X-ray reflections from the calcite of the Currant Creek locality.

In general, the calcite of normal calcareous sediments is virtually free of Mg. This holds for the older rocks made up of fossil remains (Chave, 1952, 1954b), as well as for cavity fillings, replacement deposits, and other calcites crystallized at low temperatures or in the zone of weathering, as evidenced from numerous X-ray patterns taken in the process of this investigation. Samples of calcite from three deep-sea cores all showed Mg-free calcite. The samples were taken from the top of the cores down to depths of as much as 9·35 metres, the cores coming from Muir Seamount (33° 42′ N, 62° 30′ W), from the Caribbean Sea (14° 59′ N, 68° 51′ W), and from a point between Africa and South America (00° 10′ N, 23° 00′ W).

Metamorphic rocks

X-ray data on a variety of metamorphic carbonates are presented in Table 4. This table contains only those specimens for which the X-ray spacings deviated from those of pure calcite by a measurable amount ($> \sim 0{\cdot}5$ mol per cent $MgCO_3$).*

* Calcites from a number of localities, not listed in Table 4, were observed to have X-ray spacings indicative of solid solution. These specimens have not been analyzed spectrographically, and because they come from areas in which the writers suspect enrichment in Fe and/or Mn, the possibility exists that the observed solid solution may be in large part due to Fe and Mn, in addition to Mg. These localities include Ducktown, Tennessee; Klodeberg, Norway; Crestmore, California; Ouray, Colorado; Phillipsburg, Montana; and Hanover, New Mexico.

Only those specimens having Mg substitutions greater than ~5 mol per cent can be used to indicate temperatures at which magnesian calcites are in equilibrium with dolomite, because of the limits of the experimental curve (Fig. 4, Graf and Goldsmith, 1955). However, a number of the specimens contain rather high concentrations of $MgCO_3$, several up to ~9 mol per cent. This amount of substitution, if stable at the time of formation, corresponds to a temperature of ~600°C, assuming that the CO_2 pressure is high enough to prevent decomposition of dolomite and that there is a sufficient amount of Mg present to produce dolomite in equilibrium with the magnesian calcite (Graf and Goldsmith, 1955, Fig.4). If there is not enough Mg in the system to form dolomite, the temperatures obtained from Fig. 4 will be *minimum* temperatures. At 600°C, dolomite decomposes at CO_2 pressures below 350 lb/in.^{2} (*ibid.*, Fig. 1). If reaction took place at CO_2 pressures insufficient to maintain dolomite but adequate to produce calcite containing 9 mol per cent $MgCO_3$, the 600°C value would represent a *minimum*, and higher temperatures would require correspondingly higher CO_2 pressures (*ibid.*, Fig. 5). If noncarbonate Mg-containing phases are also present under equilibrium conditions, they will have no effect on the Mg content of the calcite as long as dolomite is present. If, however, the amount of Mg present is insufficient to form dolomite, an unknown equilibrium distribution between magnesian calcite and the noncarbonate phases will exist in the dolomite stability field, and again the amount of Mg in the calcite (*ibid.*, Fig. 4) will represent a minimum temperature. This latter type of equilibrium distribution also holds in the dolomite decomposition field.

Metamorphic carbonates commonly show the association of magnesian calcite with dolomite. Assuming that the dolomite is a product of the metamorphic process and not a later replacement,* the association is strongly suggestive of a quenched-in equilibrium, indicative of temperatures and CO_2 pressures sufficiently high to produce calcite in equilibrium with dolomite. Whether dolomite was present in the carbonate rock before metamorphism, or whether part or all of it was produced during the metamorphism, has no bearing on the equilibrium.

The fact that the calcites of some high-temperature marbles are effectively quenched from temperatures as high as ~600°C is somewhat puzzling in the light of the experimental data (Graf and Goldsmith, 1955). Equilibrium can be attained at 600°C in reasonable times in the laboratory, and although it is realized that the materials used for experimental work are exceedingly fine-grained and reactive, one might expect that during the very slow cooling that must have taken place in nature the calcites would have reverted to lower-temperature states, i.e., dolomite plus a calcite poorer in Mg, before being effectively quenched. One factor that has not been considered is the effect of total pressure on the system. If cooling proceeded at considerable depth, a very great rock pressure would act in the direction of development and preservation of phases with smaller molar volumes. The X-ray data indicate, however, that magnesian calcites apparently have the

* This appears to be a valid assumption. If dolomitization later took place, the process responsible for it would be expected to remove Mg from the magnesian calcite, which is metastable at low temperatures.

same molar volumes as the equivalent combinations of calcite and dolomite, and therefore this effect would hardly seem to be significant.

Variations in the amount of Mg in solid solution in calcite up to several percent have been observed in the same metamorphic unit, and even from within the same hand specimen. Such complex phenomena as highly local variations in impurity content (which might affect the rate of lower-temperature processes),* post-metamorphic alteration, grain size at the time of reaction, etc., could be responsible and are very difficult to evaluate.

It is likely that the observed Mg concentrations of the metamorphic calcites are not the concentrations that were in equilibrium during the highest-temperature stages of the metamorphic process. The maintenance of down-temperature equilibrium would result in exsolution of dolomite with concurrent decrease in the Mg concentration of the calcite (Fig. 4, Graf and Goldsmith, 1955). This effect might be expected in view of the reactivity of the system at elevated temperatures. If exsolution took place, but equilibrium was not strictly maintained, dolomite could be locally exsolved along with a magnesian calcite, from a host magnesian calcite that in unreacted areas retained a higher temperature Mg content. Thus, an assemblage of dolomite along with two† different magnesian calcites might be expected. A number of examples of this association are listed in Table 4.

The assemblage of dolomite and magnesian calcite(s) in itself gives no information as to how much if any of the dolomite may have formed by exsolution and how much may have been in equilibrium with magnesian calcite at elevated temperatures and CO_2 pressures. Investigation of a number of thin-sections of calcite-dolomite marbles from several localities has revealed textures suggestive of exsolution.

One particularly good example, from a granulite facies carbonate from West Greenland, is illustrated in Fig. 7. The blebs, which in this section are oriented at an angle to the traces of cleavage in the single crystal of calcite, have optical properties which suggested that they are also a carbonate phase. The particular grain shown in Fig. 7 was removed from the thin-section and examined by precession and oscillation single-crystal X-ray techniques. Three phases were observed: (1) the host calcite, giving the strongest reflections; (2) dolomite; and (3) a small amount of calcite in the same orientation as the dolomite. The amount of solid solution in the calcite could not be determined by the single-crystal techniques used. The dolomite and associated calcite were oriented with a twofold axis of each (pseudo-twofold, in the case of the dolomite) in common with a twofold axis of the host calcite. The microscopic texture, similar to that of the perthitic feldspars, and the association of dolomite and calcite in the blebs, are excellent evidence for an exsolution origin.

We have made no attempt to survey the field of metamorphic carbonates to determine how common this phenomenon may be. Exsolved dolomite might display a variety of geometrical forms of which the texture of Fig. 7 would be only one. Recrystallization during or after the exsolution might produce independent

* For example, see the effect of traces of NaCl and other salts in accelerating the thermal decomposition of dolomite (Graf, 1952).

† Although a whole series of magnesian calcites might be developed during a nonequilibrium exsolution process, two narrow compositional ranges are commonly observed; one apparently represents the host magnesian calcite, the other, the magnesian calcite being exsolved at the time an effective quench took place.

grains of dolomite and a calcite phase, so that many high-temperature marbles would contain no evidence of exsolution, even though it had taken place.

Coexisting calcites, but without dolomite as a necessary accompanying phase, may be obtained through degenerative processes such as weathering. For example, specimen 82 in Table 4 is an unweathered gray calcitic portion of a marble that grades into a weathered, salmon-coloured, Mg-free calcite. The loss of Mg by weathering is clearly shown in this single specimen. Other outcrop specimens, of granulite-facies marbles from Greenland, showed somewhat weathered, nearly Mg-free calcite associated with fresher Mg-containing calcite. The loss of Mg during a process of this sort may stop at any stage short of completion, resulting in variable Mg contents. Likewise, Chave (1952, 1954b) mentions the loss of Mg with geologic time from the skeletal parts of marine organisms. Inasmuch as diffusion is far less important than solution and redeposition at low temperatures, the absence of water is probably important for the persistence of such metastable magnesian calcites under earth-surface conditions.

Predazzites.—Predazzites and pencatites are considered to be formed from dolomitic limestones and dolomites, respectively, thermally metamorphosed so that the dolomite decomposes to calcite and periclase. The periclase may be partially or completely hydrated to brucite, $Mg(OH)_2$. As shown by Graf and Goldsmith (1955), the decomposition of dolomite may take place at a temperature as low as ~375°C, if all the CO_2 that is evolved by the reaction can be dissipated without the buildup of CO_2 pressures.

Several predazzite-type rocks were X-rayed, and those that were found to contain magnesian calcites are listed in Table 4. These specimens are from the type locality, Predazzo, Tyrol. Specimens 92 and 93 contain two magnesian calcites, one quite high in Mg, the other moderately high. The value of ~9 mol per cent $MgCO_3$ for one of the determinations on the magnesian calcite of the Tyrol predazzites would indicate that a temperature of at least 600°C had been attained. It is of interest to note that the temperature may have been higher, inasmuch as the value of ~600°C is obtained from the curve of dolomite-magnesian calcite equilibrium, and this rock was obviously in the field of magnesian calcite-periclase equilibrium. It is also of interest that the X-ray photographs of this material show a weak and somewhat diffuse (112) reflection of dolomite. It is likely that the dolomite was formed by back reaction during cooling, and it is also possible that the Mg content of the calcite was *increased* when the rock cooled down through the dolomite stability field (Fig. 5, Graf and Goldsmith, 1955). The presence in this rock of the two calcite phases may thus be a consequence of (1) conversion during cooling of a portion of the magnesian calcite that was in equilibrium with the periclase, to a more magnesian calcite; (2) nonequilibrium unmixing during cooling; or (3) incomplete rejection of Mg during later-stage katamorphic processes. Mechanism (1) would require reaction with some of the MgO to form both the more magnesian of the two calcites, and any dolomite redeveloped. In mechanisms (2) and (3) back reaction with the MgO is not necessary.

The X-ray diagram of the pencatite shows no dolomite and only 3 mol per cent $MgCO_3$ is solid solution in the calcite. Samples of predazzites (brucite marbles) from the Rutherglen district, Ontario, and from Wakefield, Quebec, contain

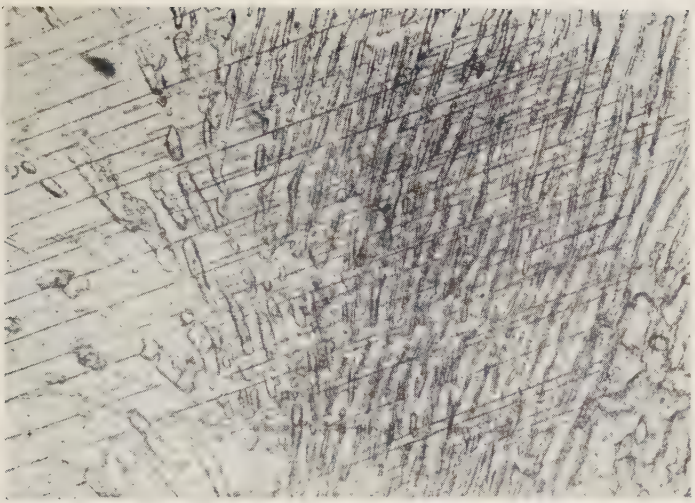

Fig. 7. Photomicrograph of dolomite blebs in calcite from granulite facies, West Greenland. Diameter of field, approximately 1 mm.

virtually Mg-free calcite in association with brucite plus some dolomite. No periclase was observed. These rocks may have (1) decomposed in the absence of water, at a low temperature near enough to 375°C so that very little Mg went into solid solution in the calcite; or (2) they may never have had a significant amount of Mg in the calcite, because hydrothermal action alone might have produced brucitic marbles by breakdown and hydration of dolomite;* or (3) if these rocks were thermally decomposed initially to MgO and calcite, later low-temperature hydrothermal action may have eliminated any substituted Mg in the calcite and may also have caused some dolomite to be redeveloped. Keith (1946) has suggested that hydrothermal activity took place in the development of the brucitic marbles of the Rutherglen district, and Faust (1949) also discusses hydrothermal action in zones of dedolomitization.

Carbonatites.—Several specimens from the Fen, Norway, and Alnö, Sweden, localities, considered by some authors to be carbonatites, were examined. Only one, No. 97 in Table 4, was found to contain a magnesian calcite. This specimen also contains a trace of dolomite, as does another Fen specimen in which the calcite has normal X-ray spacings. A specimen from Alnö, containing a dark mica, proved to be free of dolomite, and the calcite has normal spacings.

The apparent paucity of Mg in carbonatite specimens is also indicated by the chemical analyses of carbonate rocks from Alnö and the Chilwa series of Nyasaland (Smith, 1953). Thus, on the basis of the few specimens on hand, it is not possible to decide whether or not the low Mg content of the calcites results from (1) escape of CO_2 through a shallow overburden, with any available Mg taken up in other phases; or (2) the activity of hydrothermal solutions, as discussed for predazzites; or (3) lack of Mg in the environment.

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* Dolomite breaks down to calcite and $Mg(OH)_2$, in the presence of pure water under moderate pressures, at ~400°C (Schloemer, 1942). Graf and Goldsmith (unpublished data) have observed this same reaction and noted that the calcite formed is essentially Mg free.

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On the acidity and salinity of rain

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ABSTRACT

Analyses of pH, Na, K, Ca, Mg, HCO_3, Cl, SO_4, NO_3, and PO_4 are recorded for forty-two rain samples collected in the English Lake District between 14 May and 23 October 1954.

NaCl was often an important constituent, and the main source of Na, Mg, and Cl appeared to be sea-spray. SO_4 was clearly correlated with soot, and free H_2SO_4 frequently accounted for an appreciable proportion of total ions. Ca, K, and SO_4 were correlated to some extent. HCO_3 was absent from more than half the samples. NO_3 and PO_4 were usually low in concentration. Sea-spray influence appeared greatest in autumn, while industrial pollution reached its highest concentration in spring.

The ecological significance of the ions in rain is pointed out.

Introduction

Although the geochemical importance of rain has long been emphasized, its ionic composition has seldom been investigated except for Cl, SO_4, NO_3, and NH_4 (Eriksson, 1952). This paper presents six months' analyses for pH, Na, K, Ca, Mg, HCO_3, Cl, SO_4, NO_3, and PO_4 at a site in the English Lake District.

The Area

Samples were collected between 14 May and 23 October 1954 at Wise Een Tarn on Claife Heights, above the western shore of Windermere and about 50 kilometres east of the Irish Sea. Rainfall is highly variable in this region of marked relief. At Ferry House and Wraymires Hatchery, just east and west of Claife Heights, the range is between about 150 and 200 centimetres per year. Monthly fall is about 10 centimetres in spring, rising to 15–18 centimetres in autumn and winter. South-westerly winds prevail.

Methods

Rain was sampled by a polythene funnel 30 centimetres in diameter, surrounded by short stainless-steel wires for protection against birds (Egner *et al.*, 1949), and leading to a gallon polythene bottle. Whatman-541 filter papers (washed with distilled water) were tied over the end of the funnel to trap soot and insects, and were replaced after each collection. Samples averaged about 2 litres, and ranged from 0·7 to 4·5 litres. They were stored in polythene bottles.

pH was measured by glass electrode; Na and K by EEL flame photometer with Calor-gas fuel; Ca and Mg by versenate titration; HCO_3 by titration to a methyl red/bromocresol green end point buffered at pH 4·5; and Cl and SO_4 conductimetrically after ion-exchange treatments, using a method devised in this laboratory by F. J. Mackereth (in press). NO_3 was estimated by visual colorimetry with phenol-disulphonic acid, adding excess $CaCO_3$ before evaporation to neutralize the rain-acids. PO_4 was also determined by visual colorimetry, employing the usual ammonium molybdate/stannous chloride technique. A rough index to soot was obtained by grading the blackness of the filters from 0 to 5 and dividing by sample volume in litres.

Total Ions

Fig. 1 shows the modal concentration of total ions to have been slightly more than 0·1 milli-equivalents per litre. In rains of this concentration SO_4 usually exceeded Cl; at the higher levels Cl was the dominant anion. If anion and cation values for the entire period (see Table 1) are summed, the former amount to 0·165 and the latter to 0·155 milli-equivalents per litre. The slight excess of anions, much less in autumn than in spring and summer, would be balanced to some degree by NH_4.

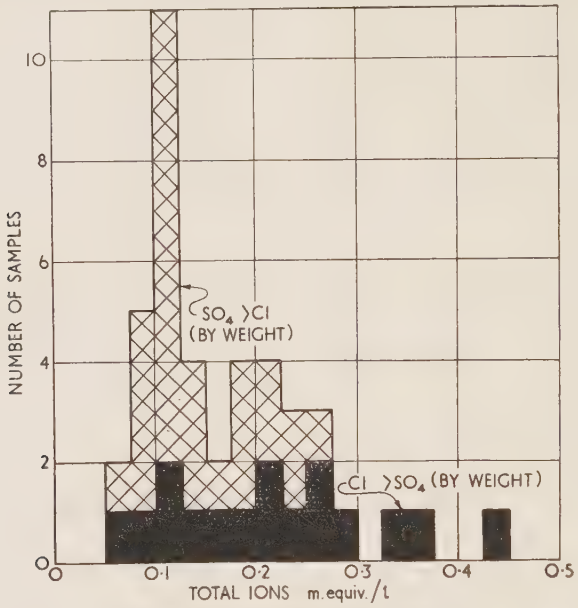

Fig. 1. Frequency distribution of total ion concentrations in Lake District rains.

Dissolved NO_3 and PO_4 usually made a negligible contribution to total ions. NO_3—N was less than 0·02 parts per million in the majority of samples, most of the higher values being encountered in spring. PO_4—P was below 0·001 parts per million in thirty-eight of forty-two samples.

Ion concentrations similar to or little greater than those of rain have been observed in pools on raised or blanket bogs in northern Britain (Gorham, in preparation), and in many upland tarns of the Lake District (F. J. Mackereth and J. Heron, private communication). Atmospheric precipitation must therefore be the principal source of nutrients for their plankton. As to the larger lakes, Windermere itself has only 0·5 milli-equivalents of total ions per litre, three times the concentration in rain. Its ionic proportions are of course very different, with Ca and HCO_3 the dominant ions.

Sodium, Magnesium, and Chloride

Na and Mg are examined in relation to Cl in Figs. 2 and 3, the straight lines representing the proportions in sea-water. The close correspondence strongly suggests derivation almost entirely from sea-spray; it may be remarked that the two highest NaCl values followed the two heaviest gales from the sea. Mechanisms

of sea-salt entry into the atmosphere have recently been much discussed (Boyce, 1951; Woodcock *et al.*, 1953; Knelman *et al.*, 1954; Kientzler *et al.*, 1954; Blanchard, 1954).

In most Lake District tarns and lakes Na and Cl are likewise present in proportions similar to that of sea-water, so that rainfall—and hence sea-spray—may be inferred as the chief source.

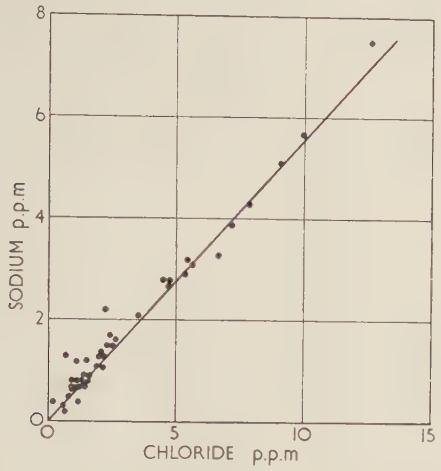

Fig. 2. The relation between sodium and chloride in Lake District rains. Straight line = proportion in sea-water.

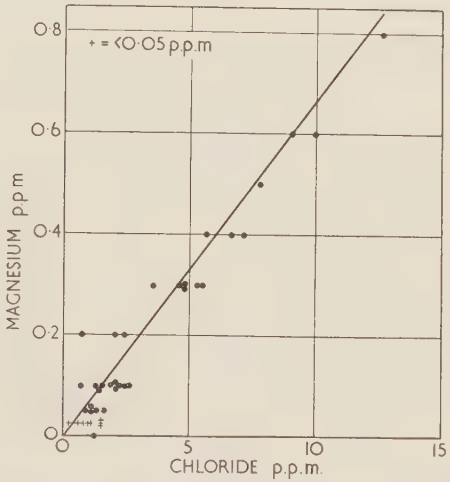

Fig. 3. The relation between magnesium and chloride in Lake District rains. Straight line = proportion in sea-water.

Even the rain highest in NaCl may not have derived its whole ion content from the sea. The ratios of H-ions and HCO_3 to Cl were far higher than in sea-water, and the ratio K : Cl was half as high again in this rain as in the sea. The ratios SO_4 : Cl and Ca : Cl were also slightly high. Alternative hypotheses might, however, be invoked. Japanese workers (Koyama and Sugawara, 1953) have postulated a differential separation of atmospheric salts by rain, hygroscopic chloride particles being washed out most easily and quickly. And Conway (1942) has inferred a supply of SO_4 by diffusion of H_2S from the muds of the continental shelf, which might perhaps account for a small amount of H_2SO_4 in rain from the sea.

The concentrations of Na, Mg, and Cl rose during the period studied, particularly in autumn. Preliminary examination of wind-speeds and directions has so far offered no clear explanation. It is hoped to investigate the matter further.

Soot, Sulphate, and Hydrogen Ions

Fig. 4 shows SO_4 plotted against Cl. While individual rains were often low in both ions, none was high in both, indicating that Cl and SO_4 came from different sources. Sea-spray has been suggested as the origin of the former, and must necessarily supply some SO_4 as well. However, a large amount of the latter ion appears to come from atmospheric pollution, as shown in Fig 5—where SO_4 is plotted versus soot index. Five samples with very little soot contamination (see Table 3) yielded an average of 1·7 parts per million of SO_4; all but one of the ten sootiest rains had

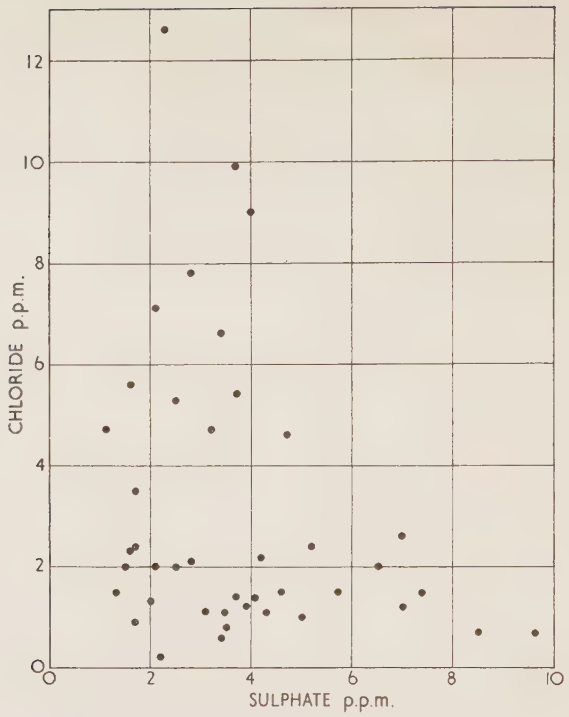

Fig. 4. Sulphate and chloride in Lake District rains.

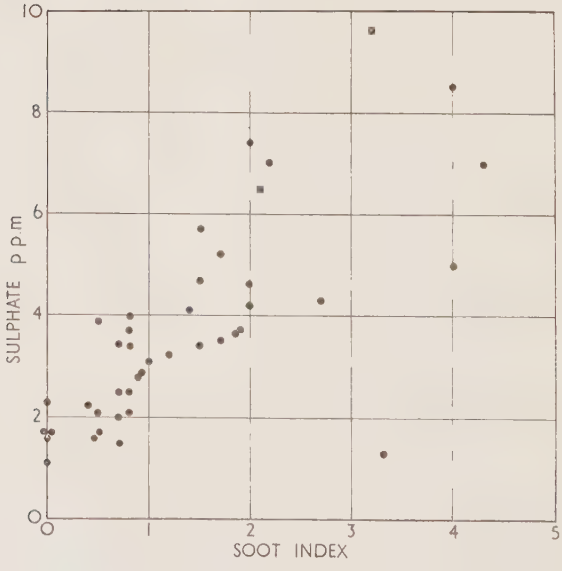

Fig. 5. The relation between sulphate and soot in Lake District rains.

more than four parts per million. It may be noted that filter contamination was always very black; on no occasion did a brown soil coloration prevail.

Fig. 6, illustrating a correlation between SO_4 and H-ion concentration, demonstrates that H_2SO_4 may be a substantial component of Lake District rains. The straight line represents equivalent proportions of the two ions. While pitting of building stone in industrial cities is well known, the writer has encountered in the

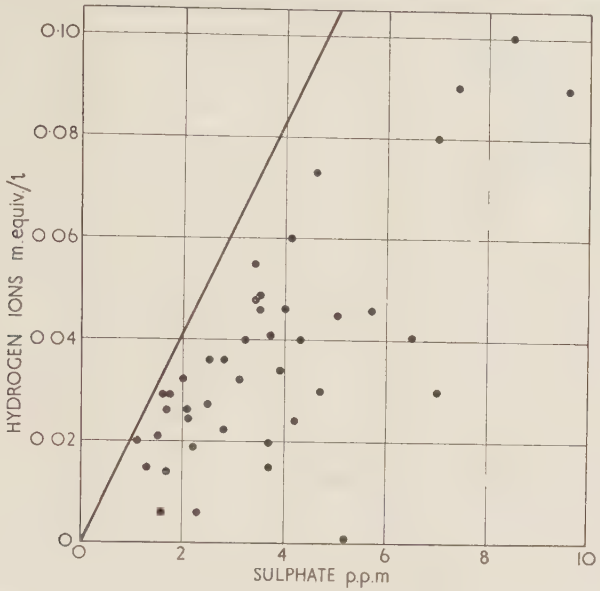

Fig. 6. Sulphuric acid in Lake District rains. Straight line = equivalent proportions of sulphate and hydrogen ions.

literature very little evidence of free mineral acid in country rain. Conway (1942) speculates that acids produced by oxidation of sulphur compounds may react with most or all of the bicarbonates deriving from dust or ash in the rain. In contrast, Tamm (1953) gives a pH range of 4·3–5·9 for rain in open fields in east Sweden, but no anion analyses.

Such a supply of dilute mineral acid must be an appreciable factor in rock and soil weathering, especially where vegetation is sparse. Moreover, if soot is the main source, its influence must have increased enormously during the past century, and be still growing. As to vegetation, two somewhat antithetical effects may be postulated. Bathing with dilute H_2SO_4 may well be inimical to many species. On the other hand, the addition of extra Ca and K in the rain, and in particular an increased degree of weathering, may lead to greater nutrient supply. While upland tarns owe most of their acidity to rain, which enters them chiefly as superficial run-off, they may also receive added Ca and K from atmospheric pollution. Lowland waters may also obtain more nutrients due to neutralization of rain-acids by bases from soil and rock minerals.

Although soot and SO_4 decrease from May to October, acidity varies rather little and is greatest in summer, because of an even larger decrease in Ca and K from the first to the middle period (see Table 1).

Comparison of the present data with figures for atmospheric precipitation in industrial cities should be of much interest. Table 2 gives analyses for pH, Ca, Cl, and SO_4 in rain subject to extreme industrial contamination. That the acidity is lower than in Lake District rains, despite a lower rainfall, is especially noteworthy. Furthermore, Cl is about half as much as SO_4 in city rain, while in the sootiest Lake District samples the concentrations of SO_4 were usually several times those of Cl. Such dissimilarity of proportions suggests a differential separation of the components of industrial pollution. Another possibility might be oxidation of sulphides in soot to H_2SO_4 while in the atmosphere. In this connection, black soot collected above a grate in which no fire had been lit for two or three weeks gave a strong odour of H_2S upon acidification.

The regression of SO_4 on Cl in Lake District tarns and lakes shows a proportionality markedly similar to the mean SO_4 : Cl ratio in rain. It may be supposed that atmospheric precipitation is the main source of both ions.

Table 1. *Ion concentrations in Lake District rain*

	Rain period				*Range in 42 individual samples*
	May 14 *to* 30 *June*	1 *July to* 31 *Aug.*	1 *Sept. to* 23 *Oct.*	*Entire period*	
Amount of rain (cm)	26	39	58	124	
*Total ions (m. equiv./*l)	0·152	0·154	0·177	0·165	0·054–0·439
pH	4·45	4·38	4·50	4·45	4·0–5·8
Na (parts per million)	1·3	1·6	2·4	1·9	0·2–7·5
K (parts per million)	0·3	0·2	0·2	0·2	0·05–0·7
Ca (parts per million)	0·5	0·2	0·2	0·3	0·1–2·0
Mg (parts per million)	0·1	0·1	0·3	0·2	nil–0·8
HCO_3 (parts per million)	0·4	0·4	0·4	0·4	nil–2·8
Cl (parts per million)	2·0	2·7	4·2	3·3	0·2–12·6
SO_4 (parts per million)	4·3	3·5	2·4	3·2	1·1–9·6
Soot index	1·5	1·3	0·7	1·0	0–4·3

Calcium, Potassium, and Bicarbonate

Fig. 7 reveals some correlation between Ca and SO_4; while Fig. 8 shows a rise in the upper limit for K with increasing SO_4 concentration. Fig. 9 further demonstrates that these two cations follow generally similar trends. While many of the sootiest rains had no more Ca and K than the purest, the highest concentrations were distinctly limited to the more contaminated samples, notably in spring. Perhaps the relatively dry spring weather, following a winter of fuel-burning, builds up atmospheric pollution at this time.

At any given SO_4 level, rains with HCO_3 naturally contain more Ca and K, since Na and Mg are commonly balanced by Cl. The source of these bicarbonates may be industrial, agricultural, or natural (i.e., soot or ash, fertilizer or dust from

cultivated fields, or dust from uncultivated ground). The highest Ca value, two parts per million, lay well above the normal regression of Ca on SO_4, due presumably to an abnormal local supply of $CaCO_3$ to the atmosphere from one of these sources.

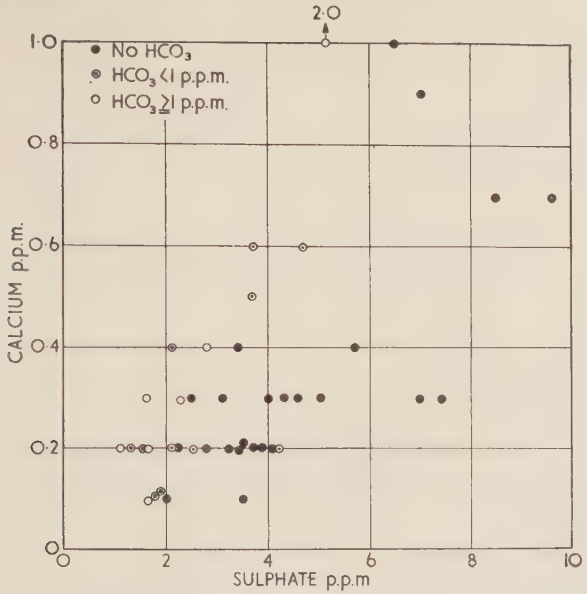

Fig. 7. Sulphate and calcium in Lake District rains with or without bicarbonate.

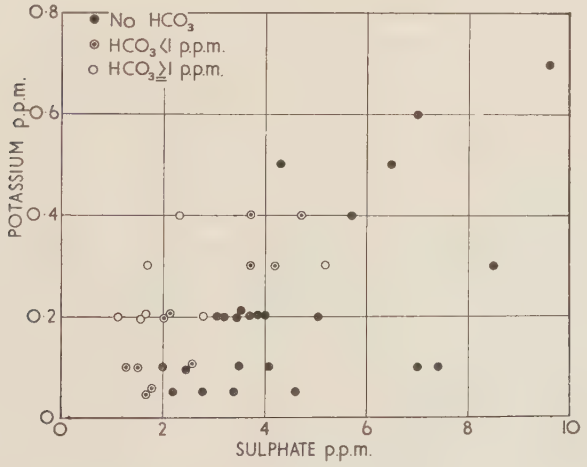

Fig. 8. Sulphate and potassium in Lake District rains with or without bicarbonate.

The ratio of Ca to SO_4 is much higher in city rains (see Table 2) than in the sootiest of the present series. Again, this may signify differential separation of atmospheric salts, or a gradual H_2SO_4 production from drifting soot.

Rain may be an important source of K for many natural bodies of water in the Lake District, in which it makes up only a small proportion of total dissolved ions.

The median K : Cl ratio for tarns and lakes is in fact somewhat less than for the present rain series. In this connection it should be borne in mind that K is subject not only to a much stronger biological demand than Cl, but also to fixation in non-exchangeable form by soil colloids.

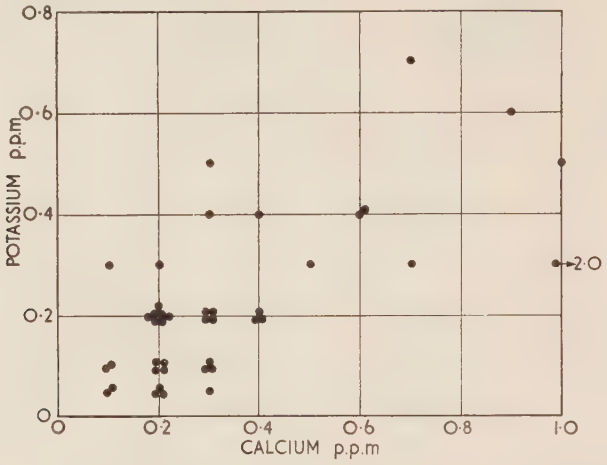

Fig. 9. The relation between calcium and potassium in Lake District rains.

*Table 2. Ion concentrations in atmospheric precipitation over industrial cities (Leeds, London, Manchester, Sheffield, Glasgow, and Newcastle, 1944–49)**

Rain (cm/yr)	*pH*	*Ca*	*Cl*	SO_4
		(parts per million)		
73	4·8	5·8	10·9	20·6

Composition of Soot-free Rain

Table 3 presents data for five rain samples on whose filters only faint traces of soot were discernible. One of these was collected after a gale from the sea. The others, while obtained after or during fairly high winds, were not exceptionally rich in NaCl, although it was the dominant component. H-ions, HCO_3, Ca, K, and SO_4 were present in much more than the proportions of sea-water (relative to NaCl). Part of the SO_4 may have originated, as previously noted, from H_2S diffusing out of the muds of the continental shelf (Conway, 1942).

H_2SO_4 was much lower, and HCO_3 much higher, than in sooty rains. At the same time Ca and K were in general lower in the clean rains, which makes it unlikely that the relatively high winds brought into the atmosphere more than the usual amount of soil-dust, rich in $CaCO_3$ and K_2CO_3. Rather it would seem that the light soot particles were more widely dispersed than usual, or settled out more

* Data provided through the courtesy of D. MacDougall, Chief Chemist, Fuel Research Station, Department of Scientific and Industrial Research.

slowly—so that the HCO_3 derived from soil particles was not neutralized by H-ions from soot.

Table 3. *Ion concentrations in five soot-free rains*

		Mean	*Range*
pH		4·8	4·5–5·2
Na	(parts per million)	3·1	1·5–7·5
K		0·2	0·05–0·4
Ca		0·2	0·1–0·3
Mg		0·3	0·05–0·8
HCO_3		1·2	0·5–2·2
Cl		5·1	2·3–12·6
SO_4		1·7	1·1–2·3

Acknowledgments—My thanks are due to A. Wilson for collecting the samples, and to J. Heron for the NO_3 and PO_4 analyses. I am greatly indebted to my colleagues, F. J. Mackereth and J. Heron, not only for advice concerning the analytical techniques, but also for much helpful discussion of the results, and especially for placing at my disposal their unpublished analyses of almost two hundred tarns and lakes in the Lake District. The Chief Chemist of the Fuel Research Station of the Department of Scientific and Industrial Research, D. MacDougall, kindly provided the data on atmospheric precipitation in industrial cities.

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A note on the isotope ratio $^{12}C/^{13}C$ in metamorphosed alum shale*

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(*Received February* 1955)

ABSTRACT

The $^{12}C/^{13}C$ ratio has been determined in alum shales from different localities in Scandinavia, i.e., in such shales having undergone thermal metamorphism. It is shown that this kind of metamorphism has not affected the isotopic composition of the alum shale.

In a recent paper (Landergren, 1954) the ratio $^{12}C/^{13}C$ has been studied i.e., in alum shales from southern Sweden. I have especially paid attention to the variations in the isotopic composition in a bore profile through the alum shale at Södra Sandby, Scania, southern Sweden, where forty-four samples from different levels of the profile have been analyzed. As seen from Table 1, the isotope ratio varies slightly both in organic and carbonate carbon (cf. also Landergren, 1954, Table 7, p. 111).

The Swedish alum shales are oil-bearing if the sediments are not metamorphosed or but slightly so, for example the alum shale from Motala, Östergötland, and from Skärlöf, Öland (see Table 2). The alum shales in Scania on the other hand have undergone a regional thermal metamorphism, further accentuated by post-Silurian diabase intrusions in this region. These shales are not oil-bearing, due to reactions caused by the regional thermal metamorphism.† Especially at Södra Sandby the alum-shale layer is penetrated by numerous diabase dykes (cf. A. H. Westergård, 1944).

Now, the question may be asked whether a thermal metamorphism of this kind has or has not affected the isotopic composition of the alum shale and/or its carbonate phase. Such an effect would be especially noticeable in the immediate vicinity of the diabase contact zone.

In order to elucidate whether the variations in the isotopic composition of the alum shale in question are connected with the diabase dykes, the figures of the ratio $^{12}C/^{13}C$ of samples of the alum shale from the diabase contact are collected in Table 1.

As seen from the table, the variations in $^{12}C/^{13}C$ from the contact zones are within the limits of variation in the isotopic composition of the whole bore profile (forty-four samples).

On comparing the average and dispersion range of $^{12}C/^{13}C$ from localities where the alum shale has undergone thermal metamorphism with the corresponding figures from localities where the shale is not metamorphosed or but slightly so we find that it is not possible to see any difference in the isotopic composition which could be connected with thermal metamorphism, as demonstrated in Table 2.

The conclusion is that neither regional nor local thermal metamorphism affects the isotopic composition of the alum shale investigated.

* Paper No. 8 in a series devoted to the application of isotope ratios to geological problems.
† Private communication from Dr. J. Eklund, Geological Survey of Sweden, Stockholm.

It should be mentioned that F. E. WICKMAN (1953) has pointed out that metamorphism has no influence of the ratio $^{12}C/^{13}C$ in a series of coal samples investigated by him.

Table 1

The isotope ratio $^{12}C/^{13}C$ in organic and carbonate carbon in alum shale from Södra Sandby, southern Sweden.

Level of diabase dykes (in m)	*Level of alum shale analyzed (in m)*	$^{12}C/^{13}C$* *in organic carbon I*	$^{12}C/^{13}C$* *in carbonate carbon II*	*Ratio I/II*
30·45–30·70	29·71–30·44	91·19	89·76	1·016
	30·72–31·35	91·07	89·16	1·021
57·30–57·60	56·70–57·30	91·08	89·37	1·019
	57·65–58·00	90·98	89·50	1·017
93·30–107·00	92·00–93·30	91·16	89·38	1·020
Average of the above samples		91·09	89·38	1·019
Average of the whole profile (44 samples)		91·11 ± 0·12†	89·52 ± 0·16†	1·018 ± 0·002†

* Stockholm scale.
† In terms of standard deviation.

Table 2

*A survey of the $^{12}C/^{13}C$ ratio in alum shale from sundry localities.**

Locality	$^{12}C/^{13}C$‖ *average*	$^{12}C/^{13}C$‖ *dispersion range*
Motala, Östergötland, Sweden†	91·16	91·03–91·30
Skärlöf, Öland, Sweden†	91·21	91·16–91·24
Södra Sandby, Scania, Sweden‡	91·11	90·84–91·37
Andrarum, Scania, Sweden‡	91·04	90·95–91·12
Gislövshammar, Scania, Sweden¶	91·06	90·00–91·12
Oslo field, Norway¶	91·09	91·04–91·11

* Private communication from Dr. J. EKLUND regarding the stage of metamorphism.
† Slightly or not metamorphosed.
‡ Thermometamorphosed and penetrated by diabase dykes.
¶ Thermometamorphosed.
‖ Stockholm scale.

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The principles governing trace-element behaviour during magmatic crystallization

Part II. The role of complex formation

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ABSTRACT

Ions with charges of four or more, and also some trivalent ions, form complexes with oxygen and hydroxyl in the magma. It is necessary to study the properties of the complex as a whole rather than the properties of the individual ion, in order to predict its behaviour. In most cases the complexes are not readily accepted into silicate minerals, and hence become enriched in residual magmas, eventually reaching a concentration which is sufficient to precipitate them in the form of primary minerals. This often occurs at the pegmatitic stage of differentiation.

The influence of volatiles (in the form of $(OH)^{-1}$ and F^{-1} ions) on trace-element behaviour is discussed in terms of the constitution of silicate melts. A parent magma must possess a high initial content of volatiles if rare elements are to be concentrated in pegmatites derived from such a magma. The effect of the volatiles is to increase the solubility of accessory minerals and therefore to prevent early crystallization and separation of rare elements in the form of accessory minerals.

Ni^2, V^3, Cr^3, and Sc^3 are usually concentrated in early crystallates from a magma. However, in the presence of a large percentage of volatiles these ions may form complexes and become concentrated to some extent in residual magmas.

1. Introduction

In a previous paper (Ringwood, 1954, Part I), the author has discussed the behaviour of univalent, divalent, and some of the larger trivalent ions of trace elements during magmatic crystallization. In this paper the behaviour of ions with charges greater than three, and also of some of the smaller trivalent ions, is considered. Justification for this division lies in the fundamentally different behaviour of the two groups. The ions of the first group exist free in the magma and their behaviour during crystallization can be interpreted satisfactorily in terms of ionic radius, ionic charge, and electronegativity. The ions of the second group, however, form complexes which maintain their identity during the crystallization process. In such cases, therefore, the properties of the complex as a whole, rather than those of the central cation, determine whether or not it will be incorporated in crystallizing minerals.

2. Previous Work

Goldschmidt (1937) has suggested that zirconium and columbium may form complexes with oxygen or hydroxyl anions in magmas. He advanced this explanation to account for the fact that the Zr/Nb ratios of a large number of rocks were approximately constant. Goldschmidt (1954) also suggested that complex formation may account for the relationships observed between tantalum (also columbium) and titanium. He pointed out that Ta^5 and Nb^5 are concentrated in later Ti^4 minerals rather than the earlier ones. This is difficult to account for on the basis of ionic charge. If, however, these ions occurred as the complexes TiO_6^{-8} and NbO_6^{-7} the relationships are explained, since NbO_6^{-7} enters later because of its lower net charge.

Goldschmidt (1954) briefly discussed the role of complex formation in geochemistry. He pointed out that complex formation by small highly charged ions is of greater importance at low temperatures, rather than at magmatic temperatures. However, in certain cases complex formation must be taken into account under magmatic conditions—for example, V^5 may occur partly as the complex VO_4^{-3} under pegmatitic conditions.

Fersman (1937) considered the importance of complex formation in magmas. He pointed out that complex formation will occur in highly alkaline magmas, and that this factor may control the type of minerals which crystallize, and also the sequence of crystallization.

During recent years much progress has been made by glass chemists in the investigation of the constitution of silicate melts, and it is now possible to apply some of their results to geochemical problems, particularly those results which bear on complex formation. Accordingly, a short summary follows of relevant present knowledge regarding the constitution of silicate melts. The discussion is based upon the findings of glass chemists, e.g., Stevels (1948), Stanworth (1950), and Weyl (1951).

3. The Constitution of Silicate Melts

The silicate magma may be regarded in a first approximation as an ionic melt in which a large number of different cations compete for the available oxygen and (to a limited extent) hydroxyl anions. The affinity of the cations for the anions is governed chiefly by their relative ionic potentials (Table 1) $\left(\text{Ionic Potential} = \frac{\text{cation charge}}{\text{ionic radius}}\right)$. The cations with the highest ionic potentials tend to become surrounded by polyhedra of oxygen anions, to which they become tightly bonded.* Of these cations, Si^4 is by far the most abundant. It is found that the oxygen anions tend to group themselves tightly around the Si^4 ions, forming SiO_4^{-4} tetrahedra. Accordingly, the structure of silicate melts (and crystals) is based dominantly upon frameworks of these tetrahedra, which may be linked in different ways. The linkage of tetrahedra comes about by the sharing of oxygen anions between two tetrahedra.

In a crystal or liquid consisting of pure silica, the tetrahedra are linked by the sharing of all corner oxygens in a three-dimensional framework. When a basic oxide such as Na_2O is added to a silica melt it has the effect of breaking down this framework. The Na^1 ions possess a small ionic potential, and are unable to compete with Si^4 for the oxygen anions. As a result the sodium ions are not related to any particular oxygens, but are forced to occupy holes in the network of SiO_4 tetrahedra. Addition of O^{2-} ions means that sharing of the oxygens at some of the corners of tetrahedra becomes unnecessary, and therefore breaks down the Si—O—Si linkage between tetrahedra. As the amount of soda added to the silica is increased, more and more linkages between tetrahedra are broken, while the sodium ions disappear into the holes in the network. Finally, when the Si/O ratio = 4, all the linkages between tetrahedra are broken and the melt is composed of free SiO_4^{-4} tetrahedra and Na^{+1} ions.

* The bonds within these polyhedra are often largely covalent. However, this does not affect the validity of the following discussion, which is based upon an ionic model.

It is therefore clear that there are two fundamentally different structural positions occupied by ions in a silicate melt. On the one hand are ions possessing high ionic potentials, of which Si^4 is the typical representative. These form the centres of oxygen tetrahedra possessing various degrees of linkage, and are called

Table 1. (*Modified after* Stevels, 1948)

Relation between ionic potentials of cations and their behaviour in magmas*

Cation	*I.P.*	*Behaviour*	*Cation*	*I.P.*	*Behaviour*
Cs^1	0·60		Sc^3	3·72	
Rb^1	0·68		Th^4	3·92	
Tl^1	0·68		Sb^3	3·96	In most magmas they
K^1	0·75		V^3	4·05	behave chiefly as free ions
Ag^1	0·79		U^4	4·12	
Na^1	1·03		Fe^3	4·68	
Cu^1	1·04		Cr^3	4·77	
Li^1	1·47	Occur as free ions occupy-			
Ba^2	1·49	ing holes in network. Do	Ga^3	4·83	
Pb^2	1·67	not form complexes.	Zr^4	5·08	
Sr^2	1·79		Hf^4	5·12	
Hg^2	1·82		Sn^4	5·64	
Ca^2	2·02		Be^2	5·72	
Cd^2	2·06		Al^3	5·88	
Sn^2	2·16		Ti^4	5·88	These ions form com-
Mn^2	2·50		Ta^5	7·35	plexes, which may or may
(Rare			Nb^5	7·5	not be linked in a network.
Earths)^3	2·64–3·48		Ge^4	7·56	Stability of complexes
			V^5	8·50	decreases as ionic potent-
Zn^2	2·70	These ions maintain an	Si^4	9·52	ial of cation decreases
Fe^2	2·70	equilibrium between com-	Mo^6	9·66	
Co^2	2·78	plex- and noncomplex-	W^6	9·66	
Cu^2	2·78	forming positions. Posi-	As^5	10·85	
Ni^2	3.00	tion of equilibrium is	B^3	13.05	
Mg^2	3·04	determined principally	P^5	14·30	
Bi^3	3·12	by composition of magma	S^6	19·98	
			C^3	25·00	

* Ionic potentials calculated from Ahren's (1952) Radii.

network formers by glass chemists. The other type includes ions of low ionic potential, such as Na^1, which do not enter the network, but exist in holes between the tetrahedra—these are the *network modifiers*.

Network formers are found to include nearly all cations with charges greater than 3, and also some of the smaller trivalent ions. Ions which behave chiefly as network formers in silicate melts are Be^2, B^3, Al^3, Ga^3, Si^4, Ge^4, Ti^4, Sn^4, Zr^4, Hf^4, P^5, V^5, As^5, Nb^5, Ta^5, Mo^6, W^6. It is important to note that some of these ions, e.g., Ti^4, Zr^4, occur in crystals in higher co-ordinations than they occur in the network. The co-ordination of such ions in a crystal is determined largely by radius-ratio considerations, whereas their co-ordination in a silicate melt is determined by their ability to replace Si^4 in a liquid, the structure of which is dominantly

controlled by the linkage of SiO_4 tetrahedra. For larger ions such as Zr^4 to replace Si^4 in tetrahedral co-ordination, it is evident that the general structure of the liquid must be much looser than that of the crystal.

Network modifiers are composed mostly of univalent, divalent, and some of the larger trivalent ions. These are all characterized by low ionic potentials, and include Li^1, Na^1, K^1, Rb^1, Cs^1, Ca^2, Sr^2, Ba^2, Pb^2, Mn^2, and the trivalent rare-earth ions.

A third group of ions, consisting of Co^2, Ni^2, Zn^2, Mg^2, Cu^2, Fe^3, V^3, Cr^3, Sc^3, become distributed between the two structural positions, so that an equilibrium is reached. These ions possess ionic potentials which are intermediate between those of network formers and network modifiers. The position which they occupy depends chiefly upon the composition of the melt. In melts with a high $\frac{Si + Al}{O}$ ratio, they are unable to compete with the abundant Si^4 and Al^3 ions for the limited supply of oxygens and are therefore forced to occupy network modifying positions. Where the $\frac{Si + Al}{O}$ ratio is low, there are more oxygens available, and consequently they are able to occupy to some extent network-forming positions, as the centres of tetrahedra.

In most natural magmas, however, the $\frac{Si + Al}{O}$ ratio is such that the members of this group occur mainly as network modifiers, and therefore for most geochemical purposes they may be classed as such. However, in some magmas of extreme composition, e.g., pegmatitic and alkaline types, some of these intermediate ions may occur as network formers. This mode of occurrence possesses some interesting geochemical consequences which will be considered at a later stage. It applies chiefly to Sc^3, V^3, Cr^3, and Ni^2.

4. Relation of Complex-forming Ions to Network Formers

In the following discussion the term "complex" will be applied to the individual MO_4 groups from which the network is constructed. It is also applied to stable non-tetrahedral groups such as CO_3^{-2}, BO_3^{-3}. It has been found more convenient to continue the discussion in terms of complex formers rather than network formers. The term "network former," although it refers to the same ions that comprise complex formers, is not as useful for geochemical purposes, since it has little significance when applied to magmas which do not possess a network structure. In magmas of this kind there are sufficient O^{-2} and OH^{-1} ions present to break down the Si—O—Si links between tetrahedra, thereby breaking down the network.

The MO_4 groups, whether as individuals or as part of a network, may be regarded as complexes, since they possess a strong tendency to retain their individuality in the melt. For example, the process of crystallization of a silicate melt involves re-arrangement of individual tetrahedra, but the tetrahedra maintain their identity during the process. Individual M—O bonds in an MO_4 tetrahedron may be broken during the orientation process, but they soon reform. The stability of these complexes is controlled by the ionic potential of the central cation. Where

this is high, e.g., S^6, P^5, B^3, C^3, the resulting complex is very stable and seldom dissociates. The bonding within these complexes possesses a large covalent component due to the high polarizing power of the central cation. Ions with lower ionic potentials, e.g., Si^4, Ta^5, V^5, also form relatively stable complexes. However, breaking of individual bonds occurs more frequently—indeed this is a necessary prerequisite to flowage. The bonding within these complexes is intermediate between ionic and covalent. Ions with still lower ionic potentials, e.g., Sn^4, Ti^4, Zr^4, also form complexes, but these are not as stable, and an appreciable amount of dissociation takes place, resulting in the presence of some free M^4 ions in the magma. However, these ions behave dominantly as complex formers.

5. Complex Formation as a Factor Governing Trace Element Behaviour

A previous paper (Ringwood, 1954) has dealt with the behaviour of trace elements which occur as free ions in the magma, i.e., as network modifiers. The behaviour of complex-forming ions, however, differs fundamentally from that of the free ions, since it is controlled by the properties of the complex as a whole. Complexes which exist in the melt are retained essentially unaltered in the crystals which separate from the melt, e.g., SiO_4^{-4}, BO_3^{-3}, SO_4^{-2}, PO_4^{-3}, although they may be re-oriented. Accordingly, in any discussion of the behaviour of complex forming ions there is no justification for speaking of isolated M^x ions ($x \geqslant 3$) which do not exist; such ions must be considered as part of oxygen complexes, and the behaviour of the complexes during differentiation must be studied.

It is well known that most highly charged trace-element ions are not readily accepted into the common silicates during magmatic crystallization, but tend to accumulate in residual magmas. Wickman (1943) has attempted to explain this fact. He suggests that ions with charges greater than 3 are not accepted into silicate structures because of the difficulty in maintaining electrical neutrality in such structures. However, this argument cannot be accepted, since it implies that highly charged ions exist free in the magma. It has already been pointed out that ions with charges greater than 3 occur as complexes, and cannot be considered free in any sense.

The structures of most minerals crystallizing from magmas are based upon SiO_4^{-4} tetrahedra linked in various ways. Therefore there are only two possible roles for a trace-element complex in the magma. It may either replace SiO_4 tetrahedra in silicate minerals or be precipitated as a separate phase. The first alternative is the one at present under consideration. There are three rules which govern the diadochy between trace-element complexes and SiO_4 complexes in silicate minerals.

1. It is clear on geometrical grounds that for an MO_x complex to substitute for SiO_4 in a silicate, the complex must be a tetrahedrally co-ordinated MO_4 type. No other complexes would be accepted into a silicate structure. Therefore all complexes which are not of the MO_4 tetrahedral type tend to be concentrated in residual fractions of a crystallizing magma, eventually reaching a concentration which is sufficient to precipitate them as primary minerals.

Examples: CO_3^{-2}, BO_3^{-3}.

The other two rules apply to tetrahedral complexes.

2. The larger the charge on the central cation, the smaller will be the tendency for MO_4 complexes to replace SiO_4 tetrahedra in silicates.

Increasing the charge on M in an MO_4 complex involves a reduction in the net charge on the complex. This reduces its ionic bonding energy with respect to SiO_4^{-4} and makes it less likely to replace SiO_4^{-4}. Consequently, PO_4^{-3}, VO_4^{-3}, TaO_4^{-3}, AsO_4^{-3}, NbO_4^{-3}, WO_4^{-2}, MoO_4^{-2}, SO_4^{-2}, are not accepted readily into silicate structures, but accumulate in the residual magma until a concentration is reached such that primary minerals containing these complexes are precipitated. This usually occurs at the pegmatitic stage of differentiation.

3. The larger the size of the central cation, the smaller will be the tendency for MO_4 groups to replace SiO_4.

This rule is derived from geometrical considerations—the larger the size of a complex, the less easily is it able to fit into a structure built of SiO_4 tetrahedra.

Accordingly, GeO_4^{-4}, TiO_4^{-4}, SnO_4^{-4}, ZrO_4^{-4}, and HfO_4^{-4} become concentrated in residual magmas relatively to SiO_4^{-4}, whilst GaO_4^{-5} tends to accumulate in residual magmas relatively to AlO_4^{-5}.

The previous discussion has dealt with the overall behaviour of complex-forming ions. It should be mentioned, however, that small amounts of some of the complex-forming ions occur free in the magma. There is an equilibrium in which the complex-forming ions occur distributed between the two structural positions—as free ions and as the centres of complexes. As the ionic potential of complex-forming ions decreases, the complexes display an increasing tendency to dissociate, consequently appreciable amounts of the complex formers with low ionic potentials occur free in the magma—notably Zr^4, Hf^4, Ti^4, Ga^3. These cations are able to replace other cations in silicates, e.g., Zr^4 replaces Ca^2 in apatite and pyroxene, Ti^4 replaces Fe^3 in ferromagnesian minerals. However, this mode of occurrence is only of secondary importance. The overall behaviour of these ions is dominated by their tendency to form complexes.

Special cases

(a) *Beryllium.* Beryllium tends to occur in glasses mainly in BeO_4^{-6} tetrahedra. This is largely due to the small size of Be^2, which requires a small co-ordination. These groups, possessing a high charge, should be incorporated rather readily into silicate structures; however, it is well known that Be^2 becomes concentrated in residual magmas. The reason is apparently that because of the low charge on Be^2 the Be—O bond is fairly weak and, at the high temperatures prevailing in magmas, the BeO_4 complex is unstable.

(b) *Boron.* The B^3 ion behaves as a complex former in silicate melts. However, it occurs in two different structural positions—as the centres of BO_3^{-3} triangles and BO_4^{-5} tetrahedra. An equilibrium is maintained between the two positions. BO_3^{-3} complexes are not readily accepted into silicate minerals because of geometrical reasons (Rule 1), and consequently are concentrated in residual magmas. BO_4^{-5} complexes are, however, preferentially incorporated in silicate minerals because they possess a higher charge than SiO_4^{-4} (Rule 2). Therefore the net behaviour of B^3 in magmas is controlled by the equilibrium existing between the two structural positions. It is well known that boron tends to become concentrated

in residual pegmatic magmas. This suggests that formation of BO_3^{-3} complexes is favoured in magmas with this composition.

There is, however, a second possibility. The B^3 ion is known to have a high affinity for F^- and OH^- in silicate melts, and it is possible that it becomes preferentially co-ordinated by these ions, forming BF_4^{-1} and $B(OH)_4^{-1}$ complexes (Weyl, 1951). Because of their low charge these complexes are not accepted in silicate minerals, and accordingly boron becomes concentrated in residual magmas. If this is so it will explain the fact that basic and acidic rocks contain about the same amount of boron (Goldschmidt, 1954), whilst in pegmatites boron becomes very strongly enriched, relative to the parent rock. In other words, when magmatic differentiation proceeds under essentially dry conditions—as when an acidic magma is derived from a basic magma, there is no preferential concentration of boron in the residual acidic magma. However, when differentiation occurs in the presence of much OH^- and F^-, as when pegmatites are formed, there is a very strong concentration of boron in the residual pegmatitic magma.

It is possible that the concentration of Be^2 in pegmatitic magmas might be due to the same cause.

(c) *Uranium and thorium.* These elements occur chiefly in magmas as the ions U^4 and Th^4 with radii 0·97 Å and 1·02 Å, respectively. They are characterized by a tendency to become concentrated in residual magmas. Despite their high charge, it seems unlikely that they will behave as complex formers, because of their relatively large size, which makes it difficult to form an MO_4 tetrahedron. Accordingly, in most magmas these ions probably behave essentially as free ions. The reason they become concentrated in residual magmas is probably that suggested by Wickman (1943). They are unable to replace Ca^2 (radius 0·99 Å) in silicate minerals because of difficulty in attaining electrostatic neutrality of the structure.

6. The "Anomalous" Behaviour of Ni^2, V^3, Cr^3, and Sc^3

The behaviour of these ions in magmas is dominated by a tendency to enter early ferromagnesian minerals in excess of their concentration in the magma. Consequently, during the process of magmatic crystallization, they are largely removed from the residual magma at an early stage. However, it is sometimes observed that these ions tend to become concentrated in residual magmas during the later stages of magmatic crystallization.

Nickel is an element which is largely removed from magmas at an early stage because of its strong tendency to enter olivines and pyroxenes. Thus Wager and Mitchell (1951) found that the Ni^2 content of the Skaerguaard magma was reduced to < 1 p.p.m. at an intermediate stage of differentiation. (Ni^2 content of parent magma = 200 p.p.m.) However, during the final stages of differentiation, when a small amount of granophyre was developed, the nickel content began to rise again, reaching 8 p.p.m. The behaviour of Cr^3 and V^3 in the Skaerguaard magma was similar to that of Ni^2. They were almost completely removed at an intermediate stage of differentiation, but became concentrated at the granophyre stage.

Other examples of this contradictory behaviour could be cited. Thus nickel is sometimes concentrated in hydrothermal ore deposits genetically related to residual

acidic magmas. Furthermore, in most nickel-ore deposits genetically associated with basic rocks it is found that the nickel-bearing sulphides are concentrated and deposited at a late stage of crystallization of the parent magma. Chromium is sometimes concentrated during late stages of magmatic activity, e.g., the chromite in many ore deposits has crystallized later than the minerals of the parent ultrabasic intrusive. Vanadium is an element which is commonly concentrated in granitic pegmatites, despite its tendency to enter early ferromagnesians in abundance. Scandium also is frequently concentrated in pegmatites, although, as GOLDSCHMIDT (1954) has shown, it is mainly concentrated in the pyroxenes of basic rocks.

The fact that Ni^2, Cr^3, V^3, and Sc^3 sometimes become concentrated in residual magmas is completely contrary to their usual behaviour, and requires explanation.

In an earlier discussion (Section 3) it was pointed out that these ions can occupy either of two structural positions in a silicate melt—in network-forming or network-modifying positions. Usually an equilibrium is reached between the two. The position they occupy is largely dependent upon the composition of the magma. The composition of most magmas is such that these ions behave mainly as network modifiers. Consequently, their behaviour is characterized by preferential entry into early ferromagnesians at the expense of Fe^2 and Fe^3, and has been discussed in the first paper (RINGWOOD, 1954). Under some conditions, however, they behave as network formers, entering the network-forming MO_4 complexes.

The position which these intermediate ions occupy in a magma depends largely upon the ratio of anions—mainly $(O^{-2} + (OH)^{-1} + F^{-1})$ to $(Si^4 + Al^3)$. They have to compete with the ions of high ionic potential (chiefly Si^4 and Al^3) for the available anions, in order to form their MO_4 complexes. In most magmas there is a considerable degree of polymerization, because there are insufficient anions to allow the Al^3 and Si^4 to form separate tetrahedra. Under these conditions, where the anion supply is low the intermediate ions are unable to form their own tetrahedral complexes. Hence they behave as free ions. In magmas which are rich in volatiles, such as pegmatitic magmas, the supply of anions is much greater (because of the abundance of F^- and OH^-). Under these conditions the intermediate ions are able to form tetrahedral complexes. Because of the large size of these tetrahedra they are not accepted into silicate minerals and are therefore concentrated in residual magmas.

This analysis has some bearing upon a current petrological argument regarding the origin of acidic rocks. It is sometimes argued, e.g., WAGER and MITCHELL (1951), that intermediate and acidic rocks cannot have differentiated from a parent basic magma by means of crystallization differentiation, because of the appreciable amounts of Ni^2, V^3, and Cr^3 usually contained in these rocks. It is argued that these elements should be removed from the crystallizing basic magma at an early stage and that residual intermediate and acidic magmas should be extremely deficient in them. Because most intermediate and acidic rocks contain moderate quantities of these elements, it is claimed that they cannot have been derived from a parent basic magma by crystallization differentiation.

In view of the previous discussion, this argument should be treated with caution, since it would not necessarily apply to the differentiation of a basic magma which is rich in volatiles.

7. Some Aspects of the Geochemistry of Pegmatites

In the previous discussion it has been shown that most complex-forming ions do not enter appreciably into the major rock-forming minerals, but accumulate in residual magmas until a concentration is reached which is sufficient to precipitate them in separate minerals. In igneous rocks (apart from pegmatites) these minerals are the common accessories, such as zircon, apatite, sphene, ilmenite, monazite, rutile, magnetite, allanite, and xenotime. These accessory minerals carry the bulk of the rare earths, Ti, P, Hf, Zr, Ta, Nb, V, U, and Th, present in igneous rocks, and probably also carry much of the Mo, W, and Sn. If these elements are to become concentrated in pegmatites, the first requirement is that they must not be precipitated at an early stage of crystallization in the form of accessory minerals. Consequently, in seeking an answer to the question of why some pegmatites contain rare elements, whereas others do not, it is necessary to study the factors which control the sequence in which accessory minerals crystallize.

In granitic rocks, the order of crystallization is usually given by the Rosenbusch Rule, which states that accessory minerals such as those mentioned above are among the earliest to crystallize. Consequently, when this order of crystallization is followed, the trace elements typically concentrated in pegmatites are largely removed at an early stage of crystallization, and therefore pegmatites formed subsequently will be devoid of these elements. Thus it may be stated as a general rule that if a rare element is to be concentrated in pegmatites, it is necessary that the accessory minerals containing this element in the parent rock should separate at a late stage of crystallization or else they should not separate at all.

This rule may be illustrated by an example described by Montgomery (1950). The Harding Pegmatite, in New Mexico, contains considerable quantities of tantalum. In most parts of the granite from which the pegmatite was derived, sphene is a common accessory mineral. However, in the granite nearest to the pegmatite, sphene occurs only in very small quantities. Rankama (1944) and Sahama (1946) have demonstrated that a large part of the tantalum present in igneous rocks occurs in titanium-rich accessory minerals, such as sphene. Consequently, the enrichment of tantalum in the pegmatite is due largely to the fact that sphene had not previously crystallized to any extent from the parent magma. Elsewhere, when sphene was present, the tantalum was contained in this mineral, and none remained in the residual magma to form tantalum-bearing pegmatites.

Most nepheline syenites follow a sequence of crystallization which is contrary to the Rosenbusch Rule. In these rocks, the accessory minerals usually crystallize at a late stage. This sequence has been termed "agpaitic" by Fersman (1929) and Goldschmidt (1930). Consequently nepheline syenites, during the process of crystal fractionation, become highly enriched in rare elements. The same applies to pegmatites derived from nepheline syenites.

Fersman (1937) has suggested that the agpaitic sequence of crystallization is due to complex formation. In magmas where the content of $(Na + K) > Al$, free alkali is left over after crystallization of felspar, and consequently the residual magma becomes strongly alkaline. Because of this, ions with valencies greater than 2 are transformed into soluble complex anions. Therefore, minerals containing these ions separate at a very late stage of crystallization.

In the opinion of the author, the agpaitic sequence of crystallization is closely connected with complex formation, but not in the way FERSMAN suggests. The ratio of (Na + K) to Al is not a critical factor, since the agpaitic sequence of crystallization is displayed by most complex pegmatites derived from granitic magmas in which (Na + K) $\leqslant$ Al. In these pegmatites, the rare and accessory minerals also crystallize at a late stage, usually replacing earlier quartz and felspar. Although the $\frac{(Na + K)}{Al}$ ratio is important in determining the type of minerals which form, as GOLDSCHMIDT (1930) has shown, it does not determine the sequence in which they crystallize.

The principal factor determining the crystallization sequence of accessory minerals is the degree of polymerization of the magma. In acidic magmas there are insufficient oxygen ions to form separate SiO_4^{-4} tetrahedral complexes, and therefore the SiO_4^{-4} complexes are forced to share corners in the same way as in quartz and felspars. Other complex-forming ions such as those mentioned above are forced to behave likewise, consequently they form complexes in which the oxygen ions are shared with neighbouring SiO_4^{-4} tetrahedra.

The solubility of a mineral in a magma is controlled largely by the difference between the lattice energy of the mineral and the energy which the dispersed ions possess by virtue of their structural position in the silicate melt. This latter quantity is analogous to lattice energy, and may be regarded as the "lattice energy" of the dissolved crystal, i.e., the energy evolved when one mole of the constituent ions of the crystal separated by an infinite distance are dissolved in the liquid. For convenience, this quantity may be called the "solution energy."

The case of a crystal dissolved in water is completely analogous. The solubility is controlled by the difference between the lattice energy of the crystal and the energy of hydration of the dispersed ions.

In considering the solubility of any single mineral in different magmas, the first factor (lattice energy) remains constant, therefore the relative solubility is controlled by the second. The greater the solution energy of the crystals, the greater the solubility. In acidic magmas in which a high degree of polymerization is present, the complex-forming ions, e.g., Zr^4, form complexes which share oxygen anions with neighbouring SiO_4^{-4} tetrahedra. The solution energy of Zr^4 ions in such a position is considerably lower than when Zr^4 is able to form separate ZrO_4^{-4} or $Zr(OH)_6^{-2}$ complexes in which only a small amount of anion-sharing occurs. This is because in the first case, where sharing occurs, highly charged central cations are brought close together and the resulting repulsion lowers the solution energy. When little or no sharing occurs, the central cation is in a position which is much more stable energetically and therefore contributes a larger amount to the solution energy. Thus minerals containing that cation are more soluble. *Consequently, the solubility of accessory minerals containing multivalent elements in the magma increases as the degree of polymerization decreases.*

This conclusion is verified by the available petrological evidence. Nepheline syenite magmas possess only a relatively small degree of polymerization, because of the large amount of alkalis compared with silica contained in them. Furthermore, they are generally believed to be rich in volatiles—in particular, water, fluorine, and chlorine.

The volatiles decrease the degree of polymerization, since they provide anions which occupy similar structural positions in the magma to oxygen. Consequently, the solubility of rare elements of high valency in nepheline syenite magmas is very considerable, which explains why accessory minerals containing these elements usually crystallize at a late stage, facilitating their concentration in pegmatite.

Basaltic magmas possess a degree of polymerization intermediate between nepheline syenite and most granitic magmas. This is because of their smaller content of alkalis and volatiles compared with nepheline syenite, and their higher content of uni- and bivalent elements, and smaller silica content, compared with granitic magmas. The solubility of accessory minerals is greater in basic magmas than in acidic magmas, a fact which is well known. However, minerals such as zircon, apatite, ilmenite, and magnetite are generally less soluble in basic magmas than in nepheline syenite magmas. Both of these facts are consistent with the relative degrees of polymerization.

Most acidic magmas possess a high degree of polymerization. Consequently, accessory minerals crystallize early from such magmas, and derived pegmatites do not contain the rare elements which occur in the accessory minerals. However, some granitic magmas possess a low degree of polymerization because of the large amount of water and other volatiles they contain.

It is from acidic magmas of this type that pegmatites containing rare minerals are formed. The accessory minerals which contain most of the rare multivalent elements do not form until a late stage of crystallization, consequently these elements accumulate in the residual pegmatitic magma until they attain a high concentration. They usually remain in solution until most of the pegmatite magma has crystallized, and finally crystallize at a late stage, replacing earlier pegmatic minerals.

The above analysis explains some features of the distribution of rare elements in pegmatites. It is well known that pegmatites in the cores of granitic intrusions are seldom rich in rare elements, whereas those near the roof and margin frequently contain large concentrations. This is directly related to the water content, and, therefore, to the degree of polymerization of the parent magma. Emmons (1933) has pointed out that the volatile content in acidic intrusions is usually much greater near the roof and margins than in the interior. Consequently, near the roofs and margins, crystallization of accessory minerals is retarded, thereby allowing the concentration of rare elements in pegmatites. In the core of intrusions, crystallization of accessories occurs early, and when pegmatites are formed, the multivalent rare elements are not found.

8. Conclusion

In the preceding pages, aspects of the geochemistry of a number of elements have been dealt with according to the theoretical principles suggested. No attempt has been made to furnish a complete treatment. The geochemistry of some elements can be well understood according to the original Goldschmidt Rules, e.g., Li, Rb, Ba, and that of a number of other elements is insufficiently known to warrant detailed consideration.

Finally, the rules governing trace-element behaviour which were discussed in

this and the preceding paper may be summarized. They may be regarded as an extension of the original Goldschmidt Rules. The rules are stated according to their order of importance.

A. *Noncomplex-forming ions*

These include the univalent, divalent, and the larger trivalent ions.

(a) For any two ions to be capable of diadochy in a crystal, their ionic radii must agree to within approximately 15 per cent.

(b) Whenever diadochy in a crystal is possible between two elements possessing appreciably different electronegativities, the element with the smaller electronegativity is preferentially incorporated.

(c) When two ions possessing similar charges and electronegativities are capable of diadochy in a crystal, the ion with the smaller radius is usually preferentially incorporated.

(d) When two ions are capable of diadochy in a crystal, the ion with the higher charge is relatively concentrated in the early crystallates, providing there is not a substantial difference in electronegativity.

B. *Complex-forming ions*

These include ions with charges greater than 3, and also some of the smaller trivalent ions.

(a) Ions forming non-tetrahedral complexes are not readily incorporated by silicate minerals, and hence become concentrated in residual magmas.

(b) Ions forming tetrahedral complexes—

(i) The larger the charge on the central cation, the less readily is a complex accepted into a silicate structure. Hence, complexes in which the central cation possesses a charge greater than 4 become concentrated in residual magmas.

(ii) The larger the size of the central cation, the less readily is a complex accepted into a silicate structure. Hence, complexes in which the radius of the central cation is greater than that of Si^4 become concentrated in residual magmas.

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On the carbon-13 abundance of limestones and coals

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ABSTRACT

The carbon isotopic compositions of about one hundred specimens of limestones and coals of Australian origin have been determined. Various depositional, diagenetic, and post-depositional processes which may have produced the carbon isotopic composition of the specimens are discussed. It has been shown that the observed variations in isotopic composition are not due entirely to varying depositional environments in the case of the limestones, and possibly not due entirely to differing original plant biotopes in the case of the coals. Such anomalous variations can be attributed only to changes in the isotopic composition of the hydrosphere and atmosphere from one time to another. It is suggested that the fundamental causes for these variations are the periodic diastrophisms which change the balance of the carbon cycle in the lithosphere. This would imply a definite "age-effect."

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1. Introduction

It is now well known that the isotopic composition of an element may be changed by numerous physical and chemical fractionating processes. In many cases it is possible to obtain the corresponding fractionation-factors, both by carrying out laboratory experiments and by making calculations using spectroscopic data. Agreement between the theoretical and experimental values is in general good (Urey, 1947).

In its natural geochemical cycle, an element is subject to many fractionating processes. These may often be linked with particular fractionation factors obtained by calculation or experiment. Conversely, it is possible in certain cases to estimate the fractionation factor for a particular geochemical process by a study of the natural isotopic abundances. Thus isotopic composition may serve as an index to these processes, and valuable information may be obtained for those rock-types whose geochemical histories are as yet incompletely understood.

In the case of carbon in particular, the broad outline of its isotopic distribution in nature has already been established (Craig, 1953). A comprehensive review of the work in this field of isotope geology up to 1953 is given by Ingerson (1953), and more recently Landergren (1954) and Craig (1954a, 1954b) have made further studies of the isotopic composition of marine sediments and plants respectively. There exist distinct groupings of isotope ratio with rock-type, with the groupings "heavy" marine carbonates (more C^{13}) and "light" plant and animal organic material particularly distinct. No other correlation, for example with a possible changing equilibrium of the carbon cycle with time, has been observed. The detailed study of all these individual groups which each possesses a characteristic average isotope ratio remains to be completed. The present paper is largely restricted to two of them, the marine limestones and the coals, and the results of an initial exploratory survey are presented and discussed. This survey was undertaken to examine the groups for possible systematic trends in isotope ratio, which would serve as a guide for a subsequent detailed study.

II. Experimental

1. *The mass spectrometer*

The mass spectrometer was constructed in the Physics Department of the University of Western Australia to the design of Nier (1947).

A fast oil-diffusion pump, using Apiezon oil C, followed by a constant level liquid air-trap evacuated the spectrometer instead of the mercury-diffusion pump used in the original design. With this arrangement the background contribution to ion peaks had to be frequently checked, but this disadvantage was somewhat offset by the rapid pumping speed in the region of the ion source.

Standard electrometer circuits were used for ion current measurements, and a system of manual gas switching from a standard to unknown gas enabled results to be obtained with almost the same facility as is possible with the magnetic type of gas-switch described by Wanless and Thode (1953).

Carbon was introduced into the spectrometer in the gaseous phase as carbon dioxide. Measurements were made on the ratio of the total ion current of mass 45 to that of mass 44 by allowing ions of these masses to impinge simultaneously on suitable collectors.

Results were not accepted unless measurements taken on the standard gas before and after introducing an unknown gas could be repeated to 0·1 per cent, thus reducing errors due to varying mass discrimination in the mass spectrometer.

2. *Sample preparation*

Carbon dioxide was prepared from carbonates by the method of McCrea (1950). For organic carbon, a wet-combustion method was used (Wilson *et al.*, 1948), after the organic matter had been treated with phosphoric acid to remove carbonates. Great care was taken to make sampling of the powdered specimen truly representative, and to obtain total yields of carbon dioxide.

3. *Presentation and accuracy of measurements*

The results are conveniently presented in terms of the deviation of the isotopic ratio of the sample from that of a standard gas, viz., permil deviation, as defined by the following formula:

$$\delta' = \frac{R_s - R_0}{R_0} 1{,}000,$$

where δ' = permil deviation of specimen (uncorrected for O^{17})

R_s = isotopic ratio of specimen

R_0 = isotopic ratio of standard

The value of δ' is corrected for the contribution to the mass 45 peak of the oxygen 17 isotope by multiplication by 1·067, to give the true permil deviation δ. This method of presentation is described in detail by Craig (1953). It is preferred to the absolute-ratio method, because the latter does not show small differences in isotopic abundance so clearly.

The standard gas was prepared from a pure homogeneous dolomite. No significant differences in permil deviation have yet been detected in successive preparations of this standard or of a single sample of either carbonate or organic carbon.

The overall reproducibility of measurement of the permil deviation for any specimen was $\pm 0{\cdot}25‰$, although under the most favourable operating conditions it was considerably better than this. The mean deviation from the average of a set of successive comparisons with the standard gas, taken on the one day, was often as little as $0{\cdot}1‰$, and the average value itself was reproducible on some subsequent day to within this figure, granted the same favourable conditions. The main source of error lay in extraneous instrumental fluctuations caused by instability in the d.c. amplifier and other electronic equipment.

As a large error in permil deviation was found to result from contamination of the sample or standard gas by air, the height of the oxygen peak in the spectrometer was constantly checked. Any air-leak which might have developed in the sample tubes or in the stopcocks in the gas-handling system was thus detected.

4. *Intercomparison of standards*

Previous workers have each used their own standard samples, and thus no easy comparison of results has been possible. The Standard Dolomite used in this survey was compared with a sample (designated *Z*) kindly provided by Dr. H. Craig of the Institute for Nuclear Studies, University of Chicago, which had been measured by this author with respect to his own standard, *Belemnitella americana*. It was was then possible to convert all the results obtained in this survey to permil deviations with respect to Craig's standard, on which scale they are presented in Tables 1 to 10.

The experimental results of the intercomparison are as follows:

Permil deviation of *Z* : $+2{\cdot}8_8$ (2/9/54)
$+2{\cdot}9_3$ (10/9/54), from Standard Dolomite

Permil deviation of *Z* : +2·66 from *Belemnitella americana*
(Craig, personal communication)

The two former values are each the mean of nine comparisons made by three operators. The position of Standard Dolomite with respect to *Belemnitella americana* thus becomes $-0{\cdot}2_4‰$.

III. The Marine Limestones

Before natural carbonate systems are considered, it is desirable to review the results that have been obtained for isotopic fractionation is experimental carbonate systems, and to discuss the formation of marine limestones in the light of these results.

1. *Isotopic fractionation in experimental carbonate systems*

Isotopic fractionation will accompany the several reactions which take place in the attainment of equilibrium in the system, solid carbonate : aqueous solution : gaseous atmosphere. These are:

$$H_2O + CO_2 = H_2CO_3 = H^+ + HCO_3^- = 2H^+ + CO_3^{--}$$

$$CO_3^{--}, \text{ aqueous} = CO_3^{--}, \text{ crystal lattice}$$

In the closed system in equilibrium, each component phase will possess a characteristic carbon (and oxygen) and isotopic ratio. This is the result, not only of the several exchange reactions occurring, e.g., $H_2C^{12}O_3 + HC^{13}O_3^- = H_2C^{13}O_3 + HC^{12}O_3^-$, but also of the initial isotopic ratio of the "source." The choice of source of the carbon in a system in equilibrium is rather arbitrary. However, it is conveniently thought of as a calcite crystal (of any given initial isotopic composition), which is introduced into a closed vessel with water and reacts chemically and isotopically to produce the state of the system subsequently observed.

McCrea (1950) carried out experiments on such systems to establish the inorganic oxygen-isotope temperature scale, and for one reaction, that between the carbonate ion in aqueous solution and in crystal lattice, the carbon isotope distribution was also obtained. His experiments confirm the theoretical figures for the fractionation factor α, viz.,

$$\alpha = 1{\cdot}0042 \text{ at } 0°C$$

$$\alpha = 1{\cdot}0038 \text{ at } 25°C$$

where

$$\alpha = \frac{(C^{13}O_3^{--})/(C^{12}O_3^{--}) \text{ crystal lattice}}{(C^{13}O_3^{--})/(C^{12}O_3^{--}) \text{ aqueous solution}}$$

This illustrates how the heavy isotope is concentrated in calcite when in equilibrium with carbonate ion in its aqueous solution. No other carbon isotope fractionation was examined by McCrea, and as yet, no *precise* experimental data are available for the fractionation factors for the exchange reactions between carbonate ion (aq.)—bicarbonate ion, bicarbonate ion—carbonic acid, carbonic acid—carbon-dioxide (aq.), and carbon-dioxide (aq.)—carbon-dioxide (gas).

Urey and Greiff (1935) have calculated the fractionation factor of the exchange reaction

$$C^{13}O_2 \text{ (gas)} + C^{12}O_3^{--} \text{ (aq.)} = C^{12}O_2 \text{ (gas)} + C^{13}O_3^{--} \text{ (aq.)}$$

namely,

$$\text{at } 0°C, \quad \alpha = 1{\cdot}015$$

$$\text{at } 25°C, \quad \alpha = 1{\cdot}012$$

These values were considered doubtful because of an inadequate theory of the vibrational frequencies, but even if the absolute values may be incorrect, they indicate that the gaseous phase is depleted in C^{12} when in isotopic equilibrium with the carbonate-water solution, and show the direction and approximate magnitude of the temperature coefficient of fractionation. For a clear illustration of the above results, it is best to use the C^{13} enrichment terminology of Craig (1954). The permil enrichment of phase A with respect to phase B is defined as

$$\varepsilon‰ = \frac{R_A - R_B}{R_B} \cdot 1000,$$

where

$$R = C^{13}/C^{12}.$$

If this is positive, phase A is "heavier," that is, it contains a greater proportion of C^{13} than phase B. Since $\varepsilon‰$ reduces to $(\alpha - 1)1000$, where α is the fractionation-factor, the equilibrium distribution of isotopes in an experimental carbonate system may now be expressed as follows: Calcite is 4·2‰ heavier than carbonate ion (aq.) at 0°C, which in turn is roughly 15‰ heavier than gaseous carbon-dioxide at the same temperature. At 25°C, the calcite is 3·8‰ heavier than carbonate ion, and the gas some 12‰ lighter.

It is necessary to examine now the isotopic compositions of the various phases of the system with respect to that of the "source," that is, the calcite crystal which reacted with water in the closed vessel to produce the above system. This is clearly a problem of calcium carbonate solubility.

2. *Calcium carbonate solubility*

In addition to the changes of fractionation due to the temperature dependence of the fractionation factor noted above, it may be shown that the isotopic ratio of a calcite crystal in equilibrium with a solution will also alter with the solubility of the calcium carbonate, even though the total amounts of the constituents of the system remain constant (i.e., in a "closed" system).

Fig. 1. Change of isotopic ratio in calcite with solubility.
(Ratio indicated by intensity of shading.)

Garrels and Dreyer (1952), who report the results of experimental investigations of calcium carbonate solubility, have shown that the solubility in natural solutions changes with five important variables: temperature, pressure, added salts, pH, and total amount of carbon dioxide in the solution; the effects of which are substantially independent of each other. They found that:

(i) Solubility decreases with increase of temperature;

(ii) Solubility increases with increase of pressure;

(iii) Solubility increases markedly with decreasing pH;

(iv) Solubility increases with addition of salts to the solution;

(v) Solubility is strongly dependent upon the amount of dissolved carbon dioxide; increase of carbon dioxide at constant pH will decrease the solubility.

A change in any of these variables will alter the solubility, and, in the closed calcite crystal—solution system, will cause deposition or solution of calcite. In such a system, for isotopic equilibrium, the C^{13}/C^{12} ratio must be less in the solution A, than in the calcite crystal B (Fig. 1a), i.e., the crystal is heavier than the solution. If now the solubility of calcium carbonate in the solution is decreased, e.g., by heating, a fresh layer of calcite C will precipitate (Fig. 1b). This will have initially the same isotopic composition as the solution from which it was precipitated and will therefore be appreciably lighter than the original calcite beneath it. This

means that it will be too light for isotopic equilibrium with the solution, and an isotopic exchange reaction will ensue in which the deposit will become heavier, C', and the solution lighter, A', until equilibrium is restored (Fig. 1c). The deposit C' must still be lighter than the original calcite B, since it is in equilibrium with a solution A' which is lighter than the solution A in equilibrium with B. The decrease of solubility has thus yielded a calcite crystal with an average composition lighter than originally, and a solution which is also lighter than at first. After a sufficient lapse of time, solid-state diffusion within the calcite will give a crystal of homogeneous isotopic composition which, being slightly heavier than C', will exchange with solution A' to give a final equilibrium as in Fig. 1d. However, the final calcite phase B' will still be lighter than B, and the solution A'' will remain lighter than A.

Thus, whether Fig. 1c or Fig. 1d be regarded as indicating the final state, it can be seen that a decrease of solubility of calcium carbonate must result in both the solid and liquid phases becoming lighter. In addition, if the decrease of solubility was due to an increase of temperature, the fractionation factor will have become slightly smaller, making the calcite crystal lighter still. A similar line of reasoning shows that increased solubility of the calcium carbonate must result in heavier solid and liquid phases.

In the foregoing, only the phases containing calcium carbonate were considered, viz., the solid and liquid phases. There will be in general also a gaseous phase containing carbon dioxide gas, in chemical and isotopic equilibrium with the carbonate and bicarbonate ions in solution, which are themselves in equilibrium with the solid calcite. Any change in the heaviness or lightness of the calcite and solution must therefore ultimately be reflected by a similar change in the isotopic composition of the gas.

All of the preceding conclusions as to changes in isotopic ratio within the calcite are of course valid only if the quantity of calcite deposited is comparable with the amount of carbonate in solution. On the other hand, the slow growth of a small crystal in a large reservoir must leave the isotopic composition of the solution substantially unchanged, and any variation in composition of successive layers deposited can only be due to actual changes of the fractionation factor itself with temperature. However, the continued precipitation of calcite, effected by any agency, and resulting in the extreme case in all the carbon of the system being deposited, must yield a calcite much lighter than the initial calcite phase.

If complete isotopic equilibrium is maintained throughout deposition by the continuous exchange between all phases, including solid-state diffusion through the crystal, the final calcite will be of homogeneous isotopic composition, with an isotopic ratio dependent upon the initial isotope abundance in the system as a whole.

If complete isotopic equilibrium is not maintained, and successive surface layers only are equilibrated with successive corresponding solutions, then by the continued exclusion of the heavy component from the system, the aqueous phase must become progressively lighter, and the last calcite layer to be deposited will be extremely light.

Turning now to the consideration of an "open" system, one in which carbon

dioxide is added to the gaseous phase, there is an increase in the total mass of the system. Such addition of carbon dioxide is accompanied by a decrease in pH. According to GARRELS and DREYER, calcium carbonate solubility decreases with the former and increases with the latter, with the net effect of increased solubility. This results in a heavier calcite phase.

The isotopic composition of the added gas itself may cause a change in the distribution of isotopes between the calcite and other phases as well as the change due to the altered chemical equilibrium. Addition of heavy carbon dioxide must result in the system as a whole becoming heavier, and similarly the system will become lighter if the added carbon dioxide is light.

3. *The relation of laboratory data to the system, sea-water—limestone*

It is clear that the oceans comprise a physico-chemical system containing carbonic acid and its ions and calcium carbonate, and possessing certain average values of pH, salinity, temperature, and pressure. The atmosphere provides the gaseous carbon dioxide phase. The interaction of these phases in natural conditions is complicated by the varying circulation of the ocean water.

For completely stagnant water where mixing takes place only by diffusion, isotopic equilibrium of the surface waters with the atmosphere is attained, and the solubility of calcium carbonate assumes a value here corresponding to the surface-water temperature, pressure, and pH. These variables alter with increasing depth, and consequently chemical and isotopic equilibrium must change continuously with depth. The mixing of water from various layers by mass-movement may thus produce a nonequilibrium system if the rate of circulation is greater than the rate at which equilibrium at a given depth can be established. According to WATTENBURG (1936), the surface waters of the ocean are constantly supersaturated with calcium carbonate. They are therefore in neither chemical nor isotopic equilibrium with atmospheric carbon dioxide and solid calcium carbonate. It follows that the present-day isotopic distribution between these phases does not represent the theoretical equilibrium distribution studied by UREY and GREIFF.

The problem of oceanic circulation has been considered by LIBBY (1951), who concludes that complete mixing of the water in the oceans takes place in something like two thousand years. Recent experimental work by KULP (1952) indicates that this is probably a minimum figure. Regarding for the moment the atmosphere, the ocean, and the limestones as a closed system, it is evident that the chemical composition of this system will attain a steady state after the elapse of a few circulation periods. An isotopic *steady state* (as distinct from the theoretical isotopic equilibrium) will be established between the gaseous and aqueous carbon phases, but not between the aqueous and solid phases. Isotope exchange in the latter takes place by the extremely slow process of solid-state diffusion, which permits the equilibration of only a very small mass of limestone during a circulation time of, say, ten thousand years. Strictly speaking, it is not justifiable to regard the system as closed, even for such a short time, geologically speaking, as the ten thousand years. To account for the existing mass of carbon-bearing sediments, it is necessary to postulate the continued addition of carbon to the system throughout geologic time. This, for simplicity, may be considered here as

the introduction of "new" carbon dioxide to the atmosphere in small constant amounts per year. Each increment of "new" carbon dioxide requires about ten thousand years for the establishement of a steady-state distribution between the gaseous and aqueous phases, with the limestone phase again strongly lagging in the attainment of steady-state isotopic composition.

Local irregularities in water circulation which exist within the hydrosphere permit the definition of small subsystems, each possessing a different isotopic distribution. These would correspond to the "local carbon dioxide cycles" of Landergren (1954). Two extreme cases are obvious: the relict seas which have little or no contact with the open ocean, and the ocean surface waters, which are rapidly and thoroughly mixed down to the limit of wave action. At this stage it is interesting to discuss some recent carbon isotope ratio determinations of the evaporites, a group of rock-types believed to result from evaporation of the water of a relict sea. Thode *et al.* (1954) found extremely light calcites in the cap-rocks of the Texas and Louisiana Salt Domes, and concluded that the calcite was formed by bacterial activity from carbon of organic origin. According to Goldman (1933), the anhydrite cap-rock of salt domes originated by the residual accumulation of sedimentary anhydrite freed from the salt by solution of the top of the dome. Of the carbonates present, only the dolomite appears clearly to be of syngenetic origin, but some of the coarse calcite crystals may be syngenetic also. The finer-grained calcite seems to be entirely epigenetic (Goldman, 1952). It is likely then that the dolomite and at least some of the calcite were chemically precipitated from solution at the same time as the anhydrite and salt, to form primary components of the evaporite bed. As this calcite occurs at the top of the bed, it must represent the last residual calcium carbonate to be precipitated. As discussed earlier, the continued chemical precipitation of calcium carbonate inevitably leads to the production of successively lighter calcites. It is, therefore, to be expected that the primary calcite of the cap-rock will be extremely light. The finer grained calcite may represent dissolved and reprecipitated primary calcite, or it may be additional calcite formed during diagenesis by the activity of bacteria. Probably it is a mixture of both, and the sum of the two effects was observed in the calcite examined by Thode.

Evidence of a much smaller subsystem which exhibits the same relationship between age of crystallization and isotopic composition is given by the vug in reef limestone containing two generations of calcite crystals, described by Wickman (1951). The matrix (which presumably is the original material of the reef limestone), the first generation of calcite, and the second generation, in this order, are progressively lighter in isotopic composition. This sequence of increasing lightness is consistent with the previous discussion of continued precipitation in a closed system.

Landergren (1954) has clearly demonstrated that the Limbata limestone was formed in two subsystems of different circulation. These were an upper subsystem of shallow, well mixed, and well aerated water, and one poorer in circulation and aeration which existed probably in the deeper parts of the "Limbata Sea." The limestones formed in each were recognized by their oxidation state, high in the former and low in the latter (so-called "reducing") environment, and the lightest

specimens of the Limbata limestone invariably came from this "reducing" subsystem. LANDERGREN'S interpretation of this, that these specimens contain calcite derived from organic carbon, appears to be fundamentally correct.

Most limestones are formed in the second extreme subsystem, the rapidly mixed ocean surface waters. According to LANDERGREN (1954), the present isotopic composition of the carbon dioxide in the atmosphere over the Atlantic Ocean is about $-9‰$ (89·3 on the Stockholm Scale), and that of marine limestones deposited in the above subsystems he estimates at $-0{\cdot}4_5‰$ (88·55). Since no analyses of present-day limestones are given, it must be presumed that this figure represents the average of the relevant Limbata limestone specimens which are of Lower Ordovician Age. It is not justified to assume a priori that the Lower Ordovician limestones have the same isotopic composition as those forming at present. Therefore LANDERGREN'S estimation for the equilibrium isotopic composition of the marine limestones is not entirely acceptable. CRAIG (1954) has measured the isotopic composition of several modern marine shells, and of these it is felt that a value of about $+1{\cdot}5‰$ (pelagic foraminifera) represents a close approach to the required equilibrium isotopic composition of modern marine limestones. The isotopic composition of the aqueous phases in ocean surface water should be represented by CRAIG'S figure for ocean bicarbonate, about -2 permils (CRAIG, 1954), but it is not known how much this value changes in regions where active precipitation of calcium carbonate is taking place. (CRAIG'S reported values show a spread of 1·6 permils.) The following picture thus evolves for the present-day distribution of the carbon isotopes in the subsystem under consideration. Solid carbonate is enriched in C^{13} by some $3\frac{1}{2}$ permils with respect to the average aqueous carbonate phase, which in turn is some 7 permils heavier than atmospheric carbon dioxide. This distribution differs from the theoretical distribution of UREY and GREIFF (1935) for the exchange between aqueous carbonate ion and gaseous carbon dioxide, due, it is believed, to the various circulation rates of the whole ocean and its smaller subsystems, and that of the atmosphere. The isotopic distribution produced by the interaction of these carbon reservoirs is best described as a "steady-state" distribution; it is certainly not the theoretical isotopic equilibrium studied by UREY and GREIFF.

It is considered that the inorganically precipitated solid carbonate phase will be enriched in C^{13} with respect to the (steady-state) aqueous carbonate phase to exactly the same degree, viz., $3{\cdot}8‰$ at 25°C, as in the experimental case studied by MCCREA. This is consistent with the approximate value of $3\frac{1}{2}‰$ previously quoted. The enrichment depends only upon the difference in molecular binding energy between the two states, crystal-lattice and aqueous ion, and failure to attain it can occur only when the carbonate is precipitated extremely rapidly, which can be effected in the laboratory but which, it is felt, finds no parallel in the ocean surface waters.

4. *The isotopic composition of calcareous shells*

Because so much of the solid carbonate in the limestones is represented by calcareous organic remains, it is necessary to consider the relationship of a secreted shell to its sea-water environment.

By the growth of shells in sea-water maintained at a constant temperature, Epstein *et al.* (1953) have established that the "organic" oxygen-isotope temperature scale is identical with the "inorganic" scale of McCrea (1950). There are no large unpredictable changes in isotopic composition caused, for instance, by changes in the rate of animal metabolism. The incorporation of the oxygen isotopes into calcareous shells proceeds in exactly the same manner as isotopic fractionation in the slow inorganic crystallization of calcite. It therefore seems beyond question that the accretion of calcium carbonate by organisms should be regarded as the "organic guidance of an inorganic process," a conclusion reached independently by Bryan and Hill (1941) for the case of the growth of hexacorals (a striking similarity of growth to spherulitic crystallization was found). Therefore, carbon isotopic distribution in shell-growth is almost certainly the same as that in slow inorganic calcite crystallization, that is at 25°C, the calcite of a living shell will be enriched in C^{13} by some 3·8‰ over the steady-state isotopic composition of carbonate ion in sea-water. Since the shells studied by Epstein *et al.* (1953) were composed largely of aragonite, it appears that there is also no significant difference in the fractionation factor at any temperature between calcite and solution, and aragonite and solution.

Epstein and Lowenstam (1953) present evidence for a threshold temperature below which an organism does not secrete its shell. The threshold is found to vary from species to species, and, in addition, there is a suggestion of a class-to-class variation: most pelecypods appear to grow in the warm temperatures, whereas most gastropods grow over the whole annual temperature range. In terms of isotopic composition, this indicates that an organism which secretes shell only in warm waters has less C^{13} than one which secretes through the whole temperature range, and less still than one which grows only in lower temperatures, because the average fractionation factor is progressively greater in these three examples. In addition, because of decreased calcium carbonate solubility in the saturated warm waters, the C^{13} abundance in the aqueous carbon phase will be diminished, and, conversely, it will be increased in the deeper colder waters. This effect enhances that of the temperature-dependent fractionation factor.

None of the carbon isotope ratio determinations so far made on living calcareous organisms is suitable for the measurement of this effect, although the wide range in isotopic composition found by Craig for modern marine invertebrates (Craig, 1953) suggests that it may be large. It may also be possible to explain Urey's results for the brachiopods, oysters, and belemnites of the English upper chalk (Urey, 1951) in terms of an effect of this kind. Brachiopods and oysters of one Zone in the Upper Chalk, living upon the sea-bed, must have shared the same aqueous carbonate phase in laying down their shells, so that the isotopic compositions of each would be expected to be very nearly identical, if it is assumed that the average isotopic composition of the aqueous carbonate phase remained constant for the duration of any one zone. However, the brachiopods appear to be heavier than the oysters, which suggests that they deposited shell material only in the colder months of the year, and the free-swimming belemnites appear to be lighter than both the oysters and brachiopods, which may indicate that they inhabited the warmer surface waters of the Cretaceous sea. Two notable exceptions

to these generalizations occur in Urey's results, which could possibly be explained by an appreciable change in the isotopic composition of the Cretaceous sea during the deposition of a single chalk zone Although these suggestions are in agreement with the believed habitats of the organisms, they do not at all agree with the work of Lowenstam and Epstein (1954) on Cretaceous palaeo-temperatures, in which the oxygen-isotope analyses are interpreted to indicate that the brachiopods deposited their shells at temperatures distinctly higher than the belemnites. Although these authors base their conclusions on more extensive observations, it is nevertheless surprising that carbon and oxygen isotope analyses should lead to such conflicting conclusions.

5. *The original isotopic composition of limestones and its preservation*

The calcareous remains of organisms, as well as inorganically precipitated calcium carbonate, are often found completely recrystallized, and frequently shells which possessed a porous mesh-like structure in the living animal are found with intimate infillings of secondary calcite. It is necessary to consider what change this might cause in the initial shell or limestone isotopic composition.

The simplest case which can be discussed is the preservation of the isotopic record in the shells of benthic animals living in clear, strongly agitated water. The calcareous remains of such organisms are found in shell-beds intercalated with sands. The shells and the shallow ocean waters which sorted then into the coarse shell-bed were in isotopic equilibrium, all organic matter was decomposed immediately by bacteria into carbon dioxide or consumed by other organisms (and thus returned to the steady-state aqueous phase in the free-moving water), and the shell-bed became consolidated by the increasing pressure of overlying sediment. Cementation was effected by solution and reprecipitation of calcium carbonate, almost in situ, by increased pressure at points of contact between the shells.

Shell and cement are in isotopic equilibrium with the sea-water in the pore-spaces, and no alteration of the C^{13} abundance in such a bed will take place unless, by subsequent diffusion or mass movement, solutions of quite different isotopic composition replace the connate water. Depth of burial and tectonic movements, however, may cause changes in isotopic composition. At high pressures the connate water will contain more carbonate ion, because of the increased solubility of calcium carbonate, and given sufficient time, the whole shell material will attain a new heavier isotopic composition. On the other hand, an increase in temperature has the opposite effect, so that the net change from the initial isotopic composition in a crystallized limestone is probably quite small.

A more complex case arises when the benthic organisms are so rapidly covered up by sediment that their fleshy organic part is decomposed in situ by bacteria, and not returned to the ocean directly. The production of carbon dioxide from this organic matter depends very largely upon the amount of available oxygen, and in most depositional environments large amounts of carbon dioxide will be introduced into the pore-space water during the diagenesis of the sediment. This tends to cause solution of the calcite, but the tendency is opposed by the rise in temperature due to biochemical heating. Sulphate-reducing and ammonifying bacteria will cause the ultimate precipitation of secondary calcite. This calcite will be

distinctly lighter than the original shell material because the carbonate ion incorporated in it has the low C^{13} abundance characteristic of its marine organic carbon origin. The dissolved carbonate in pore-space water is much too light for isotopic equilibrium with the original shell material, which now commences isotopic exchange with the solution. The "resistance" of shell material to isotope exchange depends upon its skeletal structure. Shells composed of large-grained, closely-fitted calcite crystals will exchange only very slowly, whereas those composed of a mesh of fine crystals and thus exposing a large area to the solution will exchange relatively quickly. Mathematical treatment of this problem by Urey (1951) shows that, for a crystal in the form of a cube of size as small as 1 mm, the isotopic record will be effectively unchanged by solid-state diffusion proceeding at 20°C, throughout the post-Cambrian era. Increase in temperature, however, will greatly accelerate the process. Therefore, if appreciable metamorphism of the bed has taken place, it must be expected that isotopic equilibrium between the initial shell material, the secondary calcite, and the pore-space water has been established, causing the whole bed to be of uniform lighter isotopic composition.

The inorganically precipitated limestones are composed of fine-grained aragonite sands and ooliths accumulating in a shallow, clear, well agitated environment, typified by the present-day deposition on the Bahama Banks recently described by Illing (1954). Being fine-grained, they are rather more prone to subsequent isotopic exchange than organic remains accumulating in shell-beds in the same environment. Their initial isotopic composition should be the same as that of the "organically guided" calcareous shell calcium carbonate, except for possible seasonal temperature-dependent changes, which may affect the shell composition in a slightly different manner owing to the temperature-threshold effect on shell deposition. It has been suggested that ooliths are fundamentally lighter than calcareous shells, on account of the rapid precipitation of calcium carbonate which constitutes oolith-growth (Craig, 1953). However, following Illing (1954), it appears that primary ooliths grow no faster than the average shell (very probably slower), so that ample time is available for each successive oolith layer to attain isotopic equilibrium with its aqueous environment.

As demonstrated by Landergren (1954), in stagnant, poorly aerated waters, the bottom layers will be rich in light carbon dioxide from bacterial decay of organic debris. Calcium carbonate precipitated by bacteria in such an environment will clearly be abnormally light, as will shells of the few benthic scavengers which can live in this habitat. However, the remains of pelagic organisms settling in these stagnant bottom waters will retain their isotopic composition corresponding to the surface water until solid-state diffusion establishes uniformity throughout the bed. It is evident that the initial isotopic composition of shells and calcareous muds and sands will vary with the degree of circulation, i.e., oxygenation, of their environment of deposition and, in addition, it will vary with the supply of decomposable organic matter during deposition.

A single limestone specimen should properly be considered as made up of any or all of the following components:

(i) Calcareous remains of organisms in which the isotopic distribution corresponding to their initial living environment is preserved;

(ii) Calcareous remains equilibrated with light secondary calcium carbonate, owing to susceptible shell structure and increased temperatures in the post-depositional history of the bed;

(iii) Fine calcite crystals inorganically precipitated, with isotopic composition corresponding to components (i) or (ii) above;

(iv) Fine secondary calcite, isotopically light, the amount of which is indicative of the depositional environment of the limestone.

6. *Discussion of results*

Limestones from the Tertiary, Devonian, and Cambrian Periods are particularly well represented in the results, as listed in Tables 1, 3, and 4. The specimens from each of these three Periods possess distinctly different average permil deviations.

Fig. 2. Areal distribution of specimens.

This is suggestive of an age-correlation, but, alone, it does not form conclusive proof, which can be established only by the analysis and detailed petrological examination of many more specimens.

Of the Tertiary limestones, five are taken from various horizons of the Trealla and Tulki limestone formations in the Cape Range of Western Australia. The specimens themselves are hard, white or cream, crystalline limestones often containing many foraminifera with a few molluscs and other fossils embedded in a fine-grained, dense, calcite matrix (Condon, Johnstone, and Perry, 1953). This indicates rather quiet-water deposition of inorganic aragonite mud which has entombed the unbroken, unsorted, organic remains (Hatch, Rastall, and Black, 1950, p. 162), and on subsequent lithification the unstable aragonite has recrystallized to calcite. Until the isotopic composition of the calcareous fossils has been

determined, it is impossible to estimate how much of the fine-grained matrix is light secondary calcite. Therefore it is not yet known for certain whether the very light isotopic composition of these limestones is due partly or wholly to a poorly-aerated environment of deposition, or whether it represents an initial lightness of the Lower Miocene Sea.

Since no trace of "reducing" conditions is present in the specimens, it appears that the latter explanation is more likely. The two-permil range in isotopic composition of these five specimens may represent irregular lateral variations in

Table 1. *The Tertiary limestones*

No.	*Specimen*	*Age*	*Location*	δ‰
B7	Foraminiferal coquinite	Lower Miocene	Trealla Formation, Cape Range, Western Australia	−6·0
B11	Foraminiferal coquinite	Lower Miocene	Trealla Formation (base), Cape Range, Western Australia	−7·0
B8	Calcilutite	Lower Miocene	Tulki Formation, Cape Range, Western Australia	$-6{\cdot}2_5$
B10	Calcilutite	Lower Miocene	Tulki Formation, Cape Range, Western Australia	−8·1
2/4331	Calcilutite	Lower Miocene	Tulki Formation, Cape Range, Western Australia	−6·7
TDM-1	Foraminiferal coquinite	Lower Miocene	King Island, Tasmania	−5·6
SA1	Bryozoan coquinite	Upper Oligocene	Mt. Gambier, South Australia	+1·7
B9	Calcarenite	Middle Eocene	Giralia, Western Australia	−4·9
Q6	Dolomite	(Tertiary)	Queensland	−6·6
			Average	−5·6

any one horizon, but on the other hand each measurement may be characteristic of the particular horizon in the vertical stratigraphic sequence. As the specimens range in time over some 1,500,000 years, it is quite conceivable that changes in ocean isotopic composition of sufficient magnitude to cause the above C^{13} abundance range could have occurred.

Specimen TDM-1, also of Lower Miocene age, but occurring on the opposite side of the Australian continent, is a friable, coarse-grained, very porous calcarenite containing many foraminifera, which appears to contain practically no secondary calcite. Its isotopic composition is of the same order as that of the Cape Range

crystalline limestones, and this suggests strongly that the Lower Miocene sea was unusually depleted in C^{13} over a wide area. Unfortunately, the precise age of specimen Q6 from Queensland (another area well separated from the preceding two), which also has a very negative permil deviation, is not yet known.

The permil deviation of specimen SA1 $+1{\cdot}7‰$ departs very radically from the Tertiary mean of $-5{\cdot}6‰$. The sample was composed almost entirely of well preserved bryozoan fragments with a subordinate amount of fine-grained matrix, so that the contribution to the isotopic composition of light secondary calcite must be small. Even though the rock is very porous and the bryozoa made up of small crystals, it seems unlikely that its initial isotopic composition has been lost. This is because the time available for solid-state diffusion has been relatively short (since the Upper Oligocene), and in addition no metamorphic heating of the bed which would speed up any solid-state isotopic exchange has taken place. Nevertheless, it should be pointed out that a heavy isotopic composition of the bryozoa would have resulted from isotopic equilibration following post-depositional *solution* of an initially more abundant calcite matrix. Assuming that no post-depositional exchange in SA1 has occurred, two alternative possibilities present themselves from the evidence of the Tertiary limestones. First, the specimen SA1 may be representative of a depositional environment whose steady-state isotopic distribution was radically different from that of the other Tertiary limestones. Secondly, there may have been a large difference in isotopic composition between the Lower Miocene and Upper Oligocene oceans—a difference in *time* rather than *place*.

The Cretaceous specimens are distinctly heavier than those of the Tertiary. Sample C8 falls into the range of isotopic composition determined by Urey (1951)

Table 2. The Mesozoic limestones

No.	*Specimen*	*Age*	*Location*	$\delta‰$
2/2963	Chalk	Upper Cretaceous	Dandarragan, Western Australia	$-1{\cdot}2$
C7	*Marsupites sp.*	Upper Cretaceous	Gingin, Western Australia	0·0
C8	*Bourguetocrinus sp.*	Upper Cretaceous	Gravesend, Kent, England	$+2{\cdot}0$
C6	*Pentacrinus scalaris*	Lias	Wurttemburg, Germany	$-0{\cdot}5_5$

for the English Cretaceous chalk, but the two West Australian specimens are both perceptibly lighter, which may indicate an areal difference in isotopic composition of the Upper Cretaceous ocean. Craig (1953) has suggested that the presence of microscopic algal remains, which make up most of the fine-grained calcareous matrix of chalk, may be responsible for its heavy isotopic composition. He considered that calcareous algae deposited heavier calcium carbonate than the shells of marine organisms living in the same environment. However, specimen C7,

Marsupites, is "heavier" than the type of chalk matrix in which it was embedded, and Urey's results show that the English chalk matrix may be both lighter and heavier than the fossils which it contains, but that, on the average, it is lighter. It is believed from the oxygen-isotope palaeo-temperature results (Urey, 1951; Lowenstam and Epstein, 1954) that the original isotopic composition of the English Upper Chalk is completely preserved for most fossils. Probably the chalk matrix also retains its original isotopic composition. It appears, then, that the chalk algal remains are no heavier than the brachiopods, crinoids, molluscs, and belemnites with which they are associated. The heaviness of the Cretaceous chalk therefore is not due to its algal content, and it can be due only to the heaviness of the ocean in Upper Cretaceous times.

In view of the increased likelihood that solid-state isotopic exchange might have smoothed out initial differences in isotopic composition of the components of the older limestones, several crinoid specimens of Permian, Carboniferous, and Devonian age were examined. Each plate of a living crinoid is a single calcite crystal, although the calcite is a very porous, spongy mass having a reticulate pattern. On the death of the organism, secondary calcite is added in optical continuity with that of the plate, usually filling all pores, thus forming a large continuous single crystal. The secondary calcite may be redistributed inorganic calcium carbonate of the same initial isotopic composition as the primary calcite, or it may be the light organic calcite formed in certain favourable environments by bacterial action. In the former case the crinoid plate would be particularly tenacious in preserving its initial inorganic isotopic composition; in the latter, its isotopic composition would be dependent upon the amount of light secondary calcite added, but exchange with external calcite would be strongly resisted as before.

The two Permian crinoids, C4 and C5 (Table 3), have very different isotopic compositions, C4 in fact being the lightest marine carbonate yet discovered, with the exception of the evaporite facies described by Thode (1954). The Callytharra Formation limestone from which C5 was taken is hard, crystalline, and extremely fossiliferous. In parts it has a foetid odour, but otherwise it shows no trace of organic residues. In general, deposition was rapid, and it seems likely that the organic matter from the numerous benthic organisms entombed in the limestone was decomposed in situ by bacteria, producing abundant secondary calcite. That this was the case is well illustrated by the difference in isotopic composition between the crinoid C5 and the composite limestone B6, from which is was extracted. B6 is nearly 4 permils lighter than the crinoid, due to its content of light organic calcite. It is reasonable to expect that the crinoid also contains a certain amount of light calcite, so that the initial isotopic composition of the primary calcite was heavier than the apparent value $+0{\cdot}9‰$. The extreme lightness of crinoid C4 may be due entirely to a large content of organic calcite, as its geological environment, the rapidly deposited calcareous sandstone of the Wandagee Formation, appears to be very favourable for the production of this material. There do not seem to be any figures available for the average initial porosity of a crinoid plate, so that it is impossible at present to estimate its maximum content of secondary calcite. However, if $-18‰$ is taken as the lightest possible isotopic composition of organic

calcite (CRAIG'S value (1953) for the organic carbon of modern marine invertebrates), if it is assumed that the organic carbon is finally completely converted to calcite, and if +2·0‰ taken as the isotopic composition of the primary calcitic skeleton, it follows that secondary light calcite must comprise some 70 per cent of the crinoid plate in order to produce the net value of −12·7‰ for C4. This seems excessive, and the alternative explanation, that the isotopic composition of the

Table 3. *The Upper Palaeozoic limestones*

No.	*Specimen*	*Age*	*Location*	*δ‰*
C4	*Calceolispongia multiformis*	Upper Artinskian	Wandagee Formation, Carnarvon Basin, Western Australia	−12·7
C5	Crinoid (unidentified)	Base Artinskian	Callytharra Formation, Carnarvon Basin Western Australia	+0·9
B6	Limestone	Base Artinskian	Callytharra Formation, Carnarvon Basin, Western Australia	−3·0
TDM-3	Limestone	(Permian)	Maria Island, Tasmania	+2·1
C2	*Agassizocrinus sp.*	Upper Mississippian	Chester Formation, Oklahoma, U.S.A.	+1·9
C3	*Perimistocrinus sp.*	Upper Pennsylvanian	Ochelata Formation, Oklahoma, U.S.A.	+1·2

Permian sea was much lighter when the Wandagee Formation was laid down, seems more reasonable. The specimen TDM-3, which is widely separated areally from the other Permian specimens, is reddish-grey, crystalline, and very fossiliferous, and apparently a clastic shallow-water sediment. It is heavy compared to the other Permian samples and evidently contains no light secondary calcite. Unfortunately, its position in the Permian sequence is not known.

An increasing heaviness appears in the older crinoid specimens, from +0·9‰ in the lower Permian (C5) to +2·5‰ in the Upper Devonian (C1). It is hazardous to draw conclusions from this trend alone, because the particular horizons from which the specimens were taken and their corresponding geologic environments are not precisely known, so that the possible content of secondary calcite in the specimens cannot be estimated. However, when the trend is considered in conjunction with all other specimens, it suggests that the oceans were generally heavy in Devonian times, becoming lighter through the Carboniferous to Permian times.

Of the Devonian limestones, it is believed that Q16, Q17, Q18, Q19, and perhaps B24 represent various parts of fossil reefs, and may contain therefore a large amount of calcium carbonate secreted by calcareous algae, even though no explicit mention

of the presence of algal remains can be found in the literature. If the calcareous algae preferentially deposit the heavy carbon isotope, as Craig's results (1953) seem to indicate, then the heaviness of these reef limestones, particularly of specimen Q16, may be due to their algal content, and not to a general heaviness of the Devonian ocean. However, Q18 at least contains no algal material, being composed entirely of crinoid remains. (Specimen B22 of Middle Silurian age was

Table 4. The Devonian limestones

No.	*Specimen*	*Age*	*Location*	*δ‰*
Q18	Limestone	Gedinnian	Marmor, Queensland	+0·9
Q19	Limestone	Gedinnian	Raglan, Queensland	+1·85
Q16	Limestone	Coblenzian	Rockhampton, Queensland	+4·7
Q17	Limestone	? Coblenzian	Gore, Queensland	+1·7
S2	Limestone	Coblenzian	Attunga, New South Wales	—1·2
B24	Limestone	Lower Middle Devonian	Narrengulla, New South Wales	+0·9
1/5007	Limestone	Middle or Upper Devonian	Napier Range, Kimberley Division, Western Australia	—1·7
C1	Crinoid (unidentified)	Upper Devonian	Mt. Pierre, West Kimberleys, Western Australia	+2·5
			Average	+1·2

composed entirely of algal remains, but it is not markedly heavier than the other Silurian specimens as shown in Table 5. On the other hand, specimen B12 (Cambrian, Table 5) although it is strongly silicified, and the effect of silicification on carbon isotopic composition is not yet known, is the heaviest of the ten Cambrian limestones.) Specimen S2 is thought to be a shallow-water deposit adjacent to a coral reef, as it comprises fragments of white fossiliferous limestone set in a matrix of grey sedimentary limestone. It is distinctly lighter than the other Devonian limestones (excepting specimen 1/5007, which is of uncertain age), and this may be due to a certain amount of light organic carbonate in the sedimentary limestone matrix.

The Silurian and Cambrian specimens are quite distinctly lighter in average isotopic composition than the Devonian specimens. Those from the Cambrian represent limestones accumulating in shallow epeiric seas: they have suffered no metamorphic heating and it seems quite likely that their original isotopic composition has been preserved. The Silurian and Devonian limestones have all been

regionally metamorphosed to varying degrees. This effect, however, is considered only to have smoothed out differences in C^{13} abundance between fossils and secondary calcite, rather than to have destroyed the average isotopic composition of the bed by the metasomatic introduction of new calcite.

No complete discussion of the Cambrian limestones can be given until detailed

Table 5. The Lower Palaeozoic limestones

No.	*Specimen*	*Age*	*Location*	δ‰
B22	Algal limestone	Lower Ludlow	Canberra, A.C.T.	−0·6
B23	*Heliolites*	Upper Silurian	Hume Limestone, Yass, New South Wales	$-0{\cdot}2_5$
S1	Dolomite	Upper Silurian	Mt. Knowles, New South Wales	−1·1
S3	Limestone	? Upper Silurian	Malongulli Formation, Cliefden Caves, New South Wales	−0·9
TDM-2	Limestone	Ordovician	Gunn's Plain, Tasmania	+2·0
B5	Oolitic limestone	Zone 8, Middle Cambrian	Skewthorpe Formation, N.E. of Wyndham, Western Australia	−1·3
B20	Limestone	Zone 7, Middle Cambrian	V. Creek Limestone, N.W. Queensland	−1·1
B17	Limestone	Zone 6, Middle Cambrian	Currant Bush Limestone, N.W. Queensland	−1·8
B21	Limestone	Zone 2, Middle Cambrian	Thorntonia Limestone, N.W. Queensland	$-0{\cdot}6_5$
B12	*Girvanella*	Zone 1, Middle Cambrian	Lawn Hill, Queensland	+0·6
B18	Limestone	Zone 1, Middle Cambrian	Soudan Limestone, Rankine River, Northern Territory	−2·9
B4	Limestone	Zone 1, Middle Cambrian	Negri Group, East Kimberleys, Western Australia	−2·9
B1	Limestone	Zone 1, Middle Cambrian	Montejinni Limestone, Wave Hill area, N.T.	−0·1
SA2	Marble	? Cambrian	Angaston, South Australia	$-0{\cdot}2_5$
			Cambrian average	−1·3

petrological work has provided a clearer picture of their depositional environments. However, it is of interest to observe that the lightest of Craig's specimens is a Cambrian oolitic limestone, the Warrior limestone, of permil deviation $-3{\cdot}3‰$ (Craig, 1953), which is of the same order as that of several of the Cambrian limestones examined here. Another oolitic limestone analyzed by Craig, the Mississippian Spergen limestone, has a permil deviation of $+2{\cdot}4‰$. The relative heaviness of this specimen is considered by Craig to be due to its fossil content, rather than to an age-effect of any kind. However, primary ooliths and calcareous organisms living in the same environment should have almost identical C^{13} enrichment (see p. 266). Thus the relative heaviness of the Spergen limestone would indicate that the aqueous carbonate phase from which it was precipitated was distinctly heavier than the corresponding phase in Cambrian times. Since the environment of deposition of these two samples is identical (shallow, agitated water super-saturated with calcium carbonate), it is not unreasonable to assume that they represent identical sub-systems of the palaeo-ocean circulation, from which it may be concluded that the Cambrian ocean was indeed lighter than that of the Mississippian Period.

The Cambrian limestones examined by Landergren (1954) also exhibit a distinctly light average permil deviation. Those of the Middle Cambrian, bituminous limestones are of the order $-5‰$ in isotopic composition, lighter than any examined here, but this is readily understood from the known restricted circulation of their depositional environment.

The single Ordovician specimen analyzed, TDM-2 (Table 5), is black, fine-grained, and crystalline, clearly the product of a reducing environment. It is therefore to be expected that this limestone will be of light isotopic composition, but its value in fact, $+2{\cdot}0‰$, is much heavier than that of any of the Cambrian or Silurian specimens of similar low-oxidation state. This suggests that the Ordovician ocean was unusually heavy at the time TDM-2 was deposited. Ordovician limestones examined by Landergren are also heavier on the average than those of the Cambrian or Silurian Periods, but they show fluctuations in isotopic composition of considerable magnitude. A range in isotopic composition is also displayed by the Ordovician specimens of Craig (1953), and although it is certain that a considerable portion of this variation is due to different environmental conditions, it is equally certain that the whole range of fluctuations in isotopic composition cannot be explained thus. Landergren's results for the oxidized and reduced members of the Limbata limestone show a small but significant overlap of types: some oxidized specimens have the same isotopic composition as some of the reduced type. For limestones of all ages examined in this survey, the correlation between oxidation-state (as revealed by colour) and isotopic composition is poor. Numerous examples of heavy reduced limestones and light oxidized limestones were observed. Clearly there must be at least one other factor, besides environmental control, responsible for limestone isotopic composition.

IV. The Coals

The coal specimens examined in this survey are mainly of the duro-clarain type, with a few canneloid and torbanitic types included for completeness. Several

carbonaceous shales were also examined, as well as some graphites and graphitic schists. Variations in isotopic composition will again be considered from the viewpoint of a possible change in reservoir composition with time.

1. *Coalification and isotopic fractionation*

In the process of coal-formation the palaeo-atmosphere may be regarded as the source of carbon. Atmospheric carbon dioxide is incorporated into plants by photosynthesis and returned to the atmosphere by respiration. A net accumulation of carbon takes place in the living plant, and, accompanying this, there is significant carbon isotope fractionation. Thus, the modern terrestrial plant group shows a fractionation of about —18‰. In most environments, the carbon of dead plants is returned by various modes of decay via the soil to the atmosphere. However, in special geologic circumstances, a net accumulation of plant debris takes place, for example in peat-bogs, and this accumulation, after burial and preservation by further deposition of plant organic matter as well as by sedimentation of other kinds, ultimately forms lignite, the first member of the coal series. It is entirely reasonable to expect isotopic fractionation during the decomposition of plants, and again during the chemical and physical processes which produce changes in coal rank. However, the magnitude of this fractionation is not known, although it is considered to be small. Possibly it should be regarded as a redistribution of the isotopes within the coal-seam rather than fractionation between the coal and its environment of other sediments. In view of the great dependence of coal isotopic composition upon that of its plant constituents, it is desirable first to consider the latter in more detail.

2. *Isotopic composition of modern plants*

Wickman (1952) and Craig (1953, 1954a,b) have made detailed surveys of the isotopic ratios of modern plants. For present purposes the following experimental findings are relevant:

(i) Modern plants show a range of some 8 permils in isotopic composition.

(ii) With the possible exception of the gymnosperms, there is no "vital effect" in fractionation characteristic of the one kind of plant.

(iii) The leaves are distinctly lighter than the wood of the same plant, and variations in wood isotopic composition are found within the one tree.

(iv) There is a marked correlation of isotopic composition with plant-biotope.

(v) Marine and terrestrial plants, which use bicarbonate ion, or carbon dioxide produced by hydrolysis of bicarbonate ion in their photosynthesis, are heavier than those which assimilate gaseous carbon dioxide only.

The observed spread of permil deviation may be attributed to two effects:
(a) The *biotope-effect*, in which the fractionation differs because of different ratios of the photosynthetic and respiratory rates (Craig, 1954a), and
(b) The *plant-compound effect*, in which samples of the same plant may contain different relative proportions of plant-compounds. Each plant-compound is expected to possess its own characteristic isotopic composition, which depends

only upon the carbon source and the processes by which the compound is formed within the plant. It is obvious that further variations must result if different plants form the same (homogeneous) chemical compounds by different processes or at different rates. From Craig (1954b) it appears that this is likely.

For the terrestrial plants, a coal-swamp can reasonably be regarded as a single biotope. Therefore all initial plant variations must contribute to variations in coal isotopic composition. Just as coal is chemically heterogeneous, so will it be isotopically heterogeneous. The amount of sorting of plant components is generally small for most coal-swamps. However "drift" coal may be sufficiently sorted to possess a different average isotopic composition compared to coals formed strictly "in situ." Leaves, pollen, and fine debris blown into waterpools certainly may be expected to possess a different average isotope ratio.

3. *The decomposition of plant debris*

The relative resistance to decay of such plant compounds as cellulose, lignin, protein, waxes, and resins is well known. Plant cellulose is particularly susceptible to bacterial attack, and if this compound (or series of compounds, as it is by no means chemically homogeneous) is decomposed to carbon dioxide by aerobic bacteria, the wood is left with one less component and may thus obtain a more uniform isotopic composition. Removal of cellulose and of the more volatile plant-oils could explain the smaller range in permil deviations found by Craig (1953) for fossil wood.

The very process of peat-bog accumulation itself indicates that the rate of aerobic decay has been small in comparison with the supply of plant debris. Anaerobic decay is similarly of small magnitude, but changing conditions from time to time in the history of a peat-bog may allow periods of great bacterial activity with resultant loss of carbon. This could cause a distinct change in isotopic composition at the particular level of the peat and so give rise to variations in coal isotopic composition. Unless chemical reactions taking place in the peat-bed result in a net loss in carbon, there can be no change in overall isotopic composition. Although changes in chemical rank of coal appear to be accompanied by the removal of oxygen, hydrogen, and carbon from peat in various proportions, no correlation of isotopic composition with coal-rank has been observed so far. From this it must be concluded that variations in isotopic composition due to such losses of carbon are much smaller than the variations due to the initial plant components.

4. *Coal sampling*

In view of the established variation in coal isotopic composition due to its initial plant components, bacterial decay, etc., coal must be regarded as a substance heterogeneous in C^{13} abundance. Thus its sampling is important. It is clear that vitrain, the only coal component readily available in a reasonably pure state, will reflect all initial variations in plant isotopic composition, since it represents simply the coalified wood or bark tissues of the coal-swamp vegetation. This is borne out by the results of Wickman (1953), who found a significant spread (several permils) in the isotopic composition of vitrains of very nearly the same age.

Only samples large enough to give the average isotopic composition of the seam itself can be expected to be reasonably constant in permil-deviation. Such samples would reflect the average composition of the ancient plant assemblage in the biotope, plus the changes (believed small) which may accompany diagenetic bacterial activity and post-depositional increases in coal-rank. Differences in the permil deviations of these representative samples, say, between two coal seams widely separated in space but precisely of the same age, will thus reflect differences in the type of plant-biotope in which the original peat-beds were formed. If the two seams are of different age, then difference in their average isotopic compositions could indicate either a biotope effect or an actual change in isotopic composition of the carbon dioxide source of the plant-material, the atmosphere, from one age to the next. It does not seem unreasonable to assume that most large coal-seams were formed in the same type of plant-biotope; in other words, the C^{13} depletion of the average coal-swamp plant assemblage with respect to its atmospheric source was very nearly constant. If it is assumed further that ancient plants fractionated carbon in the same manner as modern plants, so that the above C^{13} depletion between atmosphere and plant has been constant in time, it follows that changes in the average isotopic composition of coal reflect changes in palaeo-atmospheric composition.

5. *Discussion of results*

The Permian coals are shown in their successive positions in the stratigraphic column, the youngest being at the top of Table 6. It must be emphasized, however, that the precise areal correlation of the Australian Permian coals is not yet fully worked out, and the sequence shown in Table 6 cannot be accepted without question.

Samples of the one seam (Artie's Seam, Muswellbrook area, N.S.W.) from three bores separated laterally by several miles, exhibit remarkably constant isotopic composition. The average permil deviation is −23·4, with a mean deviation of 0·2‰, which is about the order of reproducibility of measurement. These results indicate that the sampling method employed is generally adequate to give the average isotopic composition of a coal-seam. The permil deviations of two samples of the Upper Liddell seam Nos. 498 and 2000, lie very close together, but two samples from the Lower Liddell seam Nos. 501 and 2396 differ by as much as two permils. Proximate analyses reveal that sample No. 501 has a lower calorific value and a higher ash content than No. 2396, so that the two samples may represent different kinds of coal.

Considering now the coals of the Muswellbrook area and the Bulli coal No. S7, whose relative position in the stratigraphic sequence is certain, and assuming that the successive coal basins represent the same kind of biotope, the differences between the average isotopic compositions of the three seams may be attributed to actual changes in atmospheric isotopic composition. The Upper Bowen Queensland series is thought to correlate with the Illawarra coal measures of New South Wales (David, 1950), and it is seen from Table 6 that samples Q4 and Q9 are identical in permil deviation with the Bulli coal (the Newcastle stage of the Illawarra coal measures). Sample Q12 is heavier, its permil deviation being close

Table 6. The Permian coals

No.	*Type and rank*	*Age*	*Location*	δ‰
S7	Duro-clarain, medium-volatile bituminous	Newcastle Age, Illawarra Coal Measures	Bulli, New South Wales	−26·2
Q4	Clarain, low-volatile bituminous	Upper Bowen Epoch	Bluff Coalfield, Queensland	−26·2
Q9	Clarain, medium-volatile bituminous	Upper Bowen Epoch	Nebo Coalfield, Queensland	−26·2
Q12	Clarain, semi-anthracite	Upper Bowen Epoch	Baralaba, Queensland	−25·5
930	Clarain, high volatile bituminous B	Tomago Age, Illawarra Coal Measures	Artie's Seam, Muswellbrook area, New South Wales	−23·4
932	Do.	Do.	Do.	−23·3
935	Do.	Do.	Do.	−22·8
1474	Do.	Do.	Do.	−23·7
1476	Do.	Do.	Do.	−23·7
1995	Do.	Do.	Do.	−23·2
1997	Do.	Do.	Do.	−23·6
1999	Do.	Do.	Do.	−23·5
2000	Clarain, high volatile bituminous C	Tomago Age	Upper Liddell Seam, Muswellbrook area	−25·6
498	Do.	Do.	Do.	−25·6
501	Do.	Do.	Lower Liddell Seam, Muswellbrook area	−24·6
2396	Do.	Do.	Do.	−22·6
Q10	Clarain, medium-volatile bituminous	Middle Bowen Epoch	Bowen Seam, Collinsville, Queensland	−21·6
Q11	Duro-clarain, high volatile bituminous	? Lower Bowen Epoch	Mt. Mulligan, Queensland	−20·8

to that of the Upper Liddell Seam in the Tomago Stage of the Illawarra coal measures. Sample Q10 of the Middle Bowen Series is appreciably older than the samples just described and it possesses a distinctly heavier isotopic composition. Sample Q11 Mt. Mulligan coal is still heavier, but its position in the stratigraphic column is uncertain. According to David (1950), the Permian beds in the Mt. Mulligan district "may be Middle Bowen, but are perhaps more likely to belong to the Upper Series" (Upper Bowen). On the other hand, Bryan and Jones (1946) place these beds in Lower Permian times, older than the Middle Bowen. If carbon isotopic composition has any age significance, this is certainly a possibility.

Table 7. The Mesozoic coals

No.	*Specimen*	*Age*	*Location*	δ‰
Q2	Clarain, high-volatile bituminous	Upper Albian (Cretaceous)	Styx Coalfield, Queensland	−26·8
Q1	Clarain	Lower Albian	Burrum Coalfield, Queensland	−27·3
Q3	Clarain, high-volatile bituminous	Jurassic	Rosewood Coalfield, Queensland	−23·8
Q8	Medium-volatile bituminous	Triassic	Ipswich Coalfield, Queensland	−22·1
Q13	Sub-bituminous	Triassic	Callide Coalfield, Queensland	−24·9
SA7	Durain sub-bituminous	Triassic	Leigh Creek, South Australia	−19·7

The Triassic coals examined in this survey (Table 7, *Mesozoic coals*) exhibit a large diversity in isotopic composition. Their areal correlation is not accurately known, and for this reason it is difficult to know what weight to place on these results. The three samples are distinctly different in rank, SA7 (Leigh Creek Coalfield) being low in the Sub-Bituminous group, Q13 (Callide Coalfield) high in the same group, and Q8 (Ipswich Coalfield) being medium to high volatile bituminous, but there is no obvious correlation here.

The two Cretaceous samples have been positioned on the international stratigraphic column (Bryan and Jones, 1946). Q1 is of Upper Aptian or Lower Albian age, and Q2 of Upper Albian age. They are both distinctly lighter than the Wealden coal analyzed by Craig (1953), which falls lower in the Cretaceous sequence (Valanginian).

All the Tertiary lignites (Table 8) are considered to be of Oligocene age, but are not necessarily contemporaneous. Three of the four samples present a reasonably constant isotopic composition, but sample SA6 is significantly heavier than the

rest. The Tertiary lignites analyzed by Craig show greater diversity, but it is not known whether these particular specimens also are contemporaneous. The heaviest of Craig's specimens is −21·6, which is close to sample SA6, −21·9. His others are both lighter than those analyzed here, but it is probable that they are also of different age (Eocene or Miocene, not Oligocene).

It is interesting to observe that for each of the three coal basins examined by Wickman (1953), the *average* values of vitrain isotopic composition were distinctly different. Although Wickman preferred the biotope-effect as an explanation for this, he admitted that evidence was insufficient to completely rule out the possibility of an age-effect.

Table 8. The Tertiary coals

No.	*Specimen*	*Age*	*Location*	*δ‰*
SA6	Lignite	Oligocene	Hd. Seymour, Co. Russell, South Australia	−21·9
SA9	Lignite	Oligocene	Moorlands, South Australia	−24·2
SA10	Lignite	Oligocene	Noarlunga, South Australia	−24·7
S5	Lignite	(Tertiary)	Ebor, New South Wales	−24·5

The two West Australian Permian coals from Irwin River and Collie, Nos. 7463 and 8133 (Table 9), are not considered contemporaneous (Fairbridge, 1953), although they possess the same isotopic composition. It may be significant that they both appear to be "drift" coals and the Collieburn Seam is distinctly sapropelic in type.

The torbanites are listed in Table 9. Two specimens from the Capertree Valley region of N.S.W., both belonging to the Newcastle Formation of the Illawarra coal measures, are separated by about 1 permil in isotopic composition. The origin of the N.S.W. torbanites has been described in detail by Dulhuntly (1944). It appears that the source of carbon in the torbanites is carbon dioxide assimilated by the constituent algae from the near-fresh water of the sheltered pools in which they grew so abundantly in Permian times. This carbon dioxide would be of three sources: atmospheric carbon dioxide in primary rain-water, bicarbonate ion from solution of limestones by river-water, and carbon dioxide produced by the decay of dead algae in the pool itself. The relative contributions from these three sources may vary from pool to pool, and certainly from time to time. It is felt that this is the explanation of the 1-permil spread of the two results. The relative stratigraphic position of the two torbanites is not known. Although *Tasmanite* was first considered to be composed of the spore-cases of a lycopodiaceous plant, its isotopic composition suggests that it is probably a torbanite similar to those of N.S.W. The specimen of *Tasmanite* examined is thought to be of Middle Bowen age. It is

about 3 permils heavier than the torbanites from the Newcastle Formation, which is in the same direction as the trend observed in the duro-clarain coals. The permil deviations of torbanites lie within range of the Marine Plant Group, −8‰ to −17‰ (Craig, 1953), which is to be expected from their known algal origin.

The specimen of *Pelionite* appears to be unique. There are marked differences between the chemical composition and physical properties of *Pelionite* and those of *Tasmanite* and the N.S.W. Torbanites, also the carbon isotopic composition is quite different. From the latter, it is evident that *Pelionite* is closely akin to the duro-clarain coals. Probably it is a type of cannel-coal.

Table 9. Specialized coal-types

No.	*Specimen*	*Age*	*Location*	*δ‰*
S6	Torbanite	Permian, Newcastle Age, Illawarra Coal Measures	Capertree Valley, New South Wales	−15·1
G3	Torbanite	Permian, Newcastle Age	Capertree Valley, New South Wales	−16·2
TDM-4	*Tasmanite*	Permian ? Greta Coal Measures Age	Latrobe, Tasmania	−12·0
TDM-9	*Pelionite*	Permian	Mt. Pelion, Tasmania	−24·7
7463	"Drift coal"	Permian	Irwin River, Western Australia	−23·1
8133	"Drift coal"	Permian	Collie, Western Australia	−23·3

The results for carbonaceous shales and graphites are listed in Table 10. Two carbonaceous shales from the Proterozoic Sturtian Series gave deviations within one-half a permil, and the values fall within the Marine Plant Group. It is therefore suggested that the carbon in these shales is of algal origin. Specimen SA5, a Proterozoic graphite occurring in metasediments from the same general region and probably of Sturtian age also, possesses an isotopic composition very close to that of the carbonaceous shales. This suggests strongly that the graphite was formed by regional metamorphism of such carbonaceous shales. The graphite S4 was formed by the metamorphism of coal-seams of Carboniferous age. This suggests that the Carboniferous coal is appreciably lighter than the Permian coals, rather than indicating that the process of graphitization may produce a lighter carbon, since according to Rankama (1954), if graphitization causes any change, it is to make the carbon a "little heavier."

The Mt. Bopple graphite Q15 was formerly believed to correlate with the Cretaceous coals of the Burrum coalfield, but the latest information places it in the Jurassic. The close agreement in isotopic composition between this graphite and that of the Jurassic coal Q3 (Table 7) lends support to this contention.

The remaining graphites represent Archaean graphitic schists from Western Australia. Assuming once more that graphitization of original sedimentary carbon does not greatly change its isotopic composition (and this is supported by the graphites Q15 and S4, both of which are of undoubted plant origin), it follows that the graphite in these meta-sediments is of biogenic origin (Rankama, 1954). Two

Table 10. *Carbonaceous shales and graphites*

No.	*Specimen*	*Age*	*Location*	δ‰
SA4	Carbonaceous shale	Sturtian Age, Proterozoic	Hd. Black Rock Plain, South Australia	−14·7
SA8	Carbonaceous shale	Sturtian Age, Proterozoic	Watervale, Co. Stanley, South Australia	−15·2
SA5	Graphite	Proterozoic (? Sturtian Age)	Hd. Barossa, Co. Adelaide, South Australia	−15·0
S4	Graphite	Carboniferous	Tenterfield, New South Wales	−26·9
Q15	Graphite	Jurassic	Mt. Bopple, Queensland	−24·3
6046	Graphitic schist	Archaeozoic	Dundas, Western Australia	−36·0
8911	Graphitic schist	Archaeozoic	Day Dawn, Western Australia	−32·8
2/4387	Graphitic schist	Archaeozoic	Coolgardie, Western Australia	−17·3

of the specimens, Nos. 6046 and 8911, are extremely light, and these may be the metamorphosed equivalents of such extremely light sediments as certain black shales which were shown by Craig (1953) to possess negative permil deviations of the same magnitude. The great difference in isotopic composition between sample No. 2/4387 and the other two graphitic schists possibly indicates a different plant-source of carbon. The absolute value of −17·3‰ is suggestive of algal material accumulating after the manner of torbanite, while the values −32·8 and −36·0 suggest marine organic matter accumulating in extreme reducing conditions. However because the process of graphitization is so poorly established, the above suggestions are tentative only. Until many more instances have been recorded in which heavy carbonates produce heavy graphites and light carbonaceous shales produce light graphites, it will be impossible to view them with much confidence.

V. The Cycle of Carbon in the Lithosphere

Recently H. Borchert (1951) has described the geochemical behaviour of the carbon-bearing materials. It is clear that the marine limestones are but one phase of the great carbon cycle in the lithosphere, and that the coals comprise a small, rather specialized branch of another phase, the organic carbon detritus in sediments of all kinds. The fixation of carbon in sedimentary rocks is followed by its mobilization in the depths of orthogeosynclines. Limestones and carbonaceous shales are granitized and assimilated by magmas, and much of their carbon returns to the atmosphere and upper lithosphere as gaseous carbon dioxide, carbonic acid solutions, and volatile hydrocarbons. Subsequent uplift of the former geosynclinal trough (mountain-building) results in intensive weathering and reworking of both unaltered and metamorphosed sediments. Thus carbon passes again into the reservoirs of the hydrosphere and the atmosphere, having travelled its full cycle. However, this is by no means a closed cycle. It is considered by Borchert that the formation of limestones in warm, shallow, epeiric seas comprises a very significant "leak" in the system. In present-day conditions at least, this carbonate leak is much greater in magnitude than the corresponding accumulation of organic carbon.

Of major importance is the time-rate at which this great carbon cycle is proceeding. In his concluding remarks, Borchert (1951) indicates that with the present rate (and average past rate) of fixation of carbon in sediments in some 250 million years hence there will be virtually no "free" carbon left in the cycle. This catastrophe has not occurred in the geologic past. It must be concluded, therefore, that "The Earth's crust breathes"—old carbon will be recycled and new carbon added within the next 250 million years. At some time in the future the rate of introduction of carbon to the reservoirs will be considerably greater than the rate of fixation of carbon in the sediments, and this has been the situation also at some time in the past. It is striking that the "life expectancy" predicted for the present cycle is of the same order of magnitude as the periodicity of such major geologic phenomena as orogenic revolutions and major glaciations.

In terms of isotopic abundance, the net accumulation of limestones means the net fixation of the heavy carbon isotope. Successive limestones through a "quiescent" period of the earth's history, when the rate of addition of new carbon or recycled old carbon is very small, will become gradually lighter as the composition of the whole reservoir slowly alters. The more ephemeral accumulations of organic carbon, however, change the reservoir composition in the direction of increasing heaviness, so that the coals and limestones will reflect the resultant of the two opposite tendencies. By increased vulcanism and rock-weathering which accompany the various phases of orogenesis, more carbon will be added to the system and the previous steady-state isotopic distribution will be changed, perhaps very appreciably. On the attainment of crustal equilibrium and the levelling of the new high relief, continued deposition of gradually lightening limestones and coal will again proceed until the beginning of another revolution of the carbon cycle. The fact that the Cambrian limestones are on the average heavier than those of the Tertiary may indicate the expected overall lightening of the systems, which would correspond to the great accumulation of limestones of all ages (regardless of any particular orogenic revolution). The change from light early Palaeozoic

limestones to heavy Devonian specimens suggests a correlation with the Caledonian Revolution, and increasing lightness from Devonian to Permian followed by heavy Mesozoic specimens may correlate with the Hercynian Orogeny.

It is interesting to observe that Landergren (1954) mentions a "tendency to periodicity" in the C^{13} abundance of specimens of Upper Ordovician limestone from a deep boring. He considered that this might synchronize with tectonic events known to have taken place about that time. It is felt that each of the individual phases of the major orogenic revolutions may have influenced the carbon isotopic composition of the sediments contemporaneously deposited. Close mapping of an extended sequence of specimens may reveal these phases, in addition to their cumulative manifestations as the major revolutions which already seem evident from the few specimens analyzed.

VI. Conclusions

The present survey has revealed large variations in the carbon isotopic composition of coals and limestones. Limestones of Lower Miocene age appear to be distinctly light, and the single Upper Oligocene specimen examined comparatively heavy. Oligocene coals are among the heavier of the coal specimens. The Devonian specimens as a group are the heaviest of the limestones, although their values show appreciable dispersion. The Cambrian specimens are lighter, with less dispersion, but not so light as those of the Tertiary Period. The Permian is marked by an extreme dispersion of limestone isotopic composition, and the Permian coals also exhibit a wide spread. However, there is evidence of regularity in the coal variations, the oldest specimens being heavy, and the youngest light. Over at least a small stratigraphic range, it appears possible to characterize each coal-seam by C^{13} abundance.

It does not seem likely that calcareous algae selectively secrete heavy carbonate, although the evidence is not wholly conclusive. Thus algae have probably not contributed to the heaviness of the Devonian reef limestones, and certainly not to the heaviness of the Cretaceous chalks. On the other hand, the lightness of other specimens appears to be due to their content of light secondary calcite, but the extreme lightness of some specimens cannot be explained in this way.

It has been pointed out in previous discussion that frequently the simplest and perhaps the only way of explaining differences in the isotopic compositions of specimens of limestones and specimens of coals is to postulate that large changes in the isotopic composition of the atmosphere and hydrosphere have taken place through geologic time. Such changes are distinct from lateral variations of isotopic composition in the one bed caused by areal differences in water-circulation, because they are exhibited by specimens from very similar environments of deposition—for example, specimens of oolitic limestone, coquinites of high oxidation state, or "in situ" duro-clarain coals of near equal rank—whose fundamental difference is age alone. It appears that these changes may be of a cyclic nature and periodic in time, and that they correlate with the major diastrophic movements that have occurred through the earth's history. Such diastrophisms maintain the great carbon cycle of the lithosphere, and changes of the latter with time cause the apparent "age-effect" in carbon isotopic composition.

It is proposed to carry out many more carbon isotope ratio analyses of selected specimens to soundly test these rather tentative conclusions. However, it is felt that the profound upheavals in the geologic past, so intimately connected as they are with the carbon cycle, must necessarily leave their mark in terms of isotopic abundances. The intriguing possibility exists of the subdivision of the Pre-Cambrian limestones in this manner, by which they may be placed in their relative stratigraphic positions between the major Pre-Cambrian Orogenic Revolutions.

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Germanium and uranium in coalified wood from upper Devonian black shale*

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ABSTRACT

Microscopic study of black, vitreous, carbonaceous material occurring in the Chattanooga shale in Tennessee and in the Cleveland member of the Ohio shale in Ohio has revealed coalified woody plant tissue. Some samples have shown sufficient detail to be identified with the genus *Callixylon*. Similar material has been reported in the literature as "bituminous" or "asphaltic" stringers.

Spectrographic analyses of the ash from the coalified wood have shown unusually high percentages of germanium, uranium, vanadium, and nickel. The inverse relationship between uranium and germanium in the ash and the ash content of various samples shows an association of these elements with the organic constituents of the coal.

On the basis of geochemical considerations, it seems most probable that the wood or coalified wood was germanium-bearing at the time logs or woody fragments were floated into the basins of deposition of the Chattanooga shale and the Cleveland member of the Ohio shale. Once within the marine environment, the material probably absorbed uranium with the formation of organo-uranium compounds such as exist in coals.

It is suggested that a more systematic search for germaniferous coals in the vicinity of the Chattanooga shale and the Cleveland member of the Ohio shale might be rewarding.

Introduction

Black, vitreous bands of carbonaceous material ($\frac{1}{8}$- to $\frac{5}{8}$-inch thick and as much as several feet long) occur in the Chattanooga shale in Tennessee and in the Cleveland member of the Ohio shale in Ohio. In descriptions of these Upper Devonian black shales, these bands have been sporadically reported as "bituminous" or "asphaltic" lenses or stringers. Stauffer (1944) described similar occurrences up to three inches thick in the Huron member of the Ohio shale in northern Ohio as "gilsonite seams." Microscopic study of the material has invariably revealed coalified woody plant tissue identical with that observed in vitrain. Some of this material shows sufficient detail of vascular pitting to be identified with the genus *Callixylon*.

Experimental Work

Nearly fresh vitrain (Breger, Meyrowitz, and Deul, 1954) collected from the top black interval of the Chattanooga shale in Davidson County, Tenn., and weathered vitrain obtained from the Cleveland member in the Bedford Reservation in Cuyahoga County south-east of Cleveland, Ohio, were available in sufficient quantities to obtain the standard coal analyses (Fieldner and Selvig, 1951) shown in Tables 1 and 2. The vitrain from the Chattanooga shale corresponds in rank to high-volatile A bituminous coal; the rank of that from the Cleveland member is probably similar, but the properties that are critical for determination of rank in this specimen have been altered by weathering. The vitrain from the Chattanooga shale is from one of the thickest bands recently observed (about half an inch). Other bands a quarter of an inch or thinner have been reported to be sparsely scattered in the shale, which contains on the average three to five thin bands in a 30-foot core in central Tennessee (Kehn, personal communication). Other streaks have been observed in the black Dunkirk shale member of the Perrysburg formation in western New York and in the black Ohio shale near Chillicothe, Ohio.

Tabular pieces of coal from the Chattanooga shale and Cleveland member of the Ohio shale

* Publication authorized by the Director, U.S. Geological Survey.

Table 1. *Analysis of vitrain from the Chattanooga shale**

	As received (%)	*Moisture-free* (%)	*Moisture- and ash-free* (%)
Proximate analysis			
Moisture	2·1	—	—
Volatile matter	40·6	41·4	42·4
Fixed carbon	55·1	56·3	57·6
Ash	2·2	2·3	—
Ultimate analysis			
Hydrogen	5·6	5·5	5·6
Carbon	77·1	78·7	80·5
Nitrogen	1·7	1·7	1·7
Oxygen	9·8	8·2	8·5
Sulphur	3·6	3·6	3·7
Ash	2·2	2·3	—
British thermal units	14,340	14,640	14,990

* Analyses by U.S. Bureau of Mines, Lab. No. E–32291, 2 February, 1954.

Table. 2. *Analysis of vitrain from the Cleveland member of the Ohio shale**

	As received (%)	*Moisture-free* (%)	*Moisture- and ash-free* (%)
Proximate analysis			
Moisture	12·7	—	—
Volatile matter	33·5	38·4	40·0
Fixed carbon	50·2	57·5	60·0
Ash	3·6	4·1	—
Ultimate analysis			
Hydrogen	5·0	4·1	4·3
Carbon	62·5	71·6	74·6
Nitrogen	1·5	1·7	1·7
Oxygen	26·4	17·4	18·2
Sulphur	1·0	1·1	1·2
Ash	3·6	4·1	—
British thermal units	10,620	12,170	12,700

* Analyses by U.S. Bureau of Mines, Lab. No. E–32292, 2 February 1954.

were cleaned with particular care to remove extraneous mineral matter before initiating geochemical studies. Spectrographic analysis (Waring and Annell, 1953) of the ash from each sample showed unusually high percentages of germanium, uranium, vanadium, and nickel (Table 3). An analysis of ash from a sample of Chattanooga shale is also shown in Table 3 for comparison.

*Table 3. Semiquantitative spectrographic analysis**

Per cent	*Ash of coal from Chattanooga shale†* *Element*	*Ash of coal from Cleveland member of the Ohio shale‡* *Element*	*Ash from Chattanooga shale§* *Element*
Over 10	Fe	Fe	Al Si
5–10	Si	Al Ca Si	Fe
1–5	Ge Al Ca V	V Ge	K
0·5–1	Ni U Mg	Co Mg Zn	Mg
0·1–0·5	Cu Ti Cr Mo Na Sr B	Cu Cr Ni Ti U	Ca Na Ti Ba
0·05–0·1	Y Pb Ba	Ba B Na Mn Sr Y	—
0·01–0·05	Co Sn Zr Mn Zn	Mo Sn Pb Zr	Co B Cu Sr Cr Mo Ni Mn
0·005–0·01	Yb	Yb	V Ga La Zr
0·001–0·005	Ga Sc Be	La Ga Sc	Y Pb Sc Ge
0·0005–0·001	—	Be	—
0·0001–0·0005	—	—	Yb Be Ag

* Analyses by Mona Frank, U.S. Geological Survey.
† Ash of coal = 1·27 per cent.
‡ Ash of coal = 1·7 per cent.
§ Ash of shale = 77·32 per cent.

Semiquantitative analyses were supplemented and confirmed by the quantitative data shown in Table 4. Analytical techniques that have already been described (Breger, Meyrowitz, and Deul, 1954) were employed to obtain percentages of moisture, ash, and uraniun in the samples. Germanium was determined quantitatively using a sodium carbonate dilution technique and appropriate standards; vanadium and nickel were determined using the pegmatite-base dilution technique described by Gordon and Murata (1952).

A small sample of Chattanooga shale from Davidson County, Tenn., containing several thin coal bands was investigated in detail to determine the relationships of germanium and uranium

in the coalified wood and in the shale. The specimen was dissected to remove four coal bands ranging from 2 to 5 mm in thickness. Five shale layers (2 to 10 mm) between the coal bands were also isolated for analysis. Four of the shale samples were highly weathered. The fifth shale sample was thicker than the others, very compact, and unweathered. Surfaces of the coal samples were cleaned of adhering mineral matter, and the individual samples were then pulverized in an agate mortar and analyzed. Analyses were shown in Table 5.

Table 4. Analysis of coals from the Chattanooga shale and the Cleveland member of the Ohio shale

	Coal from Chattanooga shale *Wt. %*	*Coal from Cleveland member of the Ohio shale* *Wt. %*
Moisture	2·3	—
Ash	1·27	1·7
Uranium in ash *	2·58	0·50
Germanium in ash†	4·0, 4·5	2·0
Vanadium in ash‡	2·90	—
Nickel in ash‡	0·36	—
Uranium in dry coal	0·033	0·0085
Germanium in dry coal	0·051, 0·057	0·034
Vanadium in dry coal	0·037	—
Nickel in dry coal	0·0046	—

* Analysis on dry basis by AUDREY SMITH, U.S. Geological Survey.
† Analyses by KATHERINE VALENTINE and MONA FRANK, U.S. Geological Survey.
‡ Analysis by A. T. MYERS, U.S. Geological Survey.

Table 5. Analyses of shale and coal bands from the Chattanooga shale

Sample	*Seq.**	*Ash* %	*Uranium*		*Germanium†*	
			In ash %	*In sample* %	*In ash* %	*In sample* %
Coal	2	4·23	0·42	0·0178	0·6	0·025
Coal	8	3·80	0·55	0·0209	2·0	0·076
Coal	6	2·45	0·57	0·0140	1·5	0·037
Coal	4	1·69	1·32	0·0223	3·0	0·051
Shale (unweathered)	1	77·32	0·0068	0·0053	0·001	0·0008
Shale	9	56·17	0·0038	0·0021	—	—
Shale	5	55·46	0·0049	0·0027	—	—
Shale	3	54·19	0·0083	0·0045	—	—
Shale	7	43·83	0·0099	0·0043	0·004	0·0018

* Numbers indicate stratigraphic sequence. No. 1 at bottom.
† Analyses by MONA FRANK, U.S. Geological Survey.

The data of Table 5 show that all the coal samples contain unusually high percentages of germanium and uranium. The ash content of each coal band is low and approximates that to be expected for vitrain (SPRUNK and O'DONNELL, 1942). Determinations of percentages of ash and uranium in the shale matrix adjacent to

these coal samples indicate a decrease in ash and uranium probably as a result of weathering. The indicated germanium content of the shale samples may be somewhat high because of the presence of very thin hair-line streaks of coal, which could not be entirely removed and which probably contribute a small amount of germanium to the shale samples.

The inverse relationship (Table 5) between uranium in the ash and the ash content of the coal samples suggests an association of uranium with the organic constituents of the coal. The same relationship is true for germanium.

Geochemical Considerations and Conclusions

The association of uranium with coalified logs or coalified woody debris has long been known (Fischer, 1950), and the occurrence of germanium in such materials has been well established (Goldschmidt, 1930; Headlee and Hunter, 1951; Aubrey, 1952; Stadnichenko, Murata, Zubovic, and Hufschmidt, 1953). An association of both uranium and germanium in the same specimen, such as has been described in this paper, has not previously been reported.

Stadnichenko, Murata, Zubovic, and Hufschmidt, in reporting on occurrences of germanium in American coals, state, "The highest concentrations of germanium have been found in coalified logs and pieces of woody coal occurring isolated in sediments." Germanium in the coalified wood from the Chattanooga shale represents another occurrence similar to those which Stadnichenko and her co-workers have described.

The germanium content of coal ash has been reported to range from less than 0·001 to 9 per cent (Headlee and Hunter, 1951; Aubrey, 1952; Stadnichenko, Murata, Zubovic, and Hufschmidt, 1953). Because germanium is frequently concentrated at the top and bottom of coal seams, it has been suggested that the element has entered the coal through the medium of ground water. Unusually high percentages of germanium may also have been introduced into ancient buried tree-stumps by the movement of ground waters. Aubrey (1952) and others (Rudge and Moon, 1946) have suggested that germanium is retained in coals in intimate association with the organic constituents rather than with the mineral matter.

The concentration of germanium in sea-water has been reported to be less than 10^{-8} per cent (Noddack and Noddack, 1939). Shales have been reported by Preuss (1940) to contain, on the average, approximately 7×10^{-4} per cent of germanium. From these data it would appear that sedimentation in a marine environment may concentrate germanium to an appreciable extent from sea-water, but the content of the element in marine sediments is considerably lower than has been found in many coals or coalified logs from fresh-water environments. The highly anomalous concentration of germanium in coalified wood from the Chattanooga shale and the Cleveland member of the Ohio shale is several orders of magnitude greater than any concentration yet noted in marine sediments and can hardly be explained on the basis of absorption from a marine environment.

As has been noted by McKelvey and Nelson (1950) and others, fine-grained shales deposited from marine environments may be uranium-bearing. Two examples of such shales are the Swedish alum shale (Eklund, 1947) and the Chattanooga

shale (McKelvey and Nelson, 1950). Sea-water contains about 2×10^{-7} per cent of uranium (Stewart and Bentley, 1954), marine formations normally contain approximately 10^{-4} per cent of uranium (Breger, 1955), and certain strata in marine formations such as the Chattanooga and Swedish alum shales are known to contain from several thousandths to several tenths of 1 per cent of uranium, indicating even greater concentration of the element from sea-water.

Several explanations are possible to account for this association of germanium and uranium, but it seems most probable that the wood or coalified wood was germanium-bearing at the time logs or woody fragments were floated into the basins of deposition of the Chattanooga shale and the Cleveland member of the Ohio shale. Once within the marine environment, the material probably absorbed uranium with the formation of organo-uranium compounds such as have been found to exist in coals (Breger, Deul, and Rubenstein, 1954).

The presence of germanium in the coalified wood from these shales suggests that a more systematic search for germaniferous coals in the vicinity of the Chattanooga shale and the Cleveland member of the Ohio shale might be rewarding.

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The convergent lead ages of the oldest monazites and uraninites (Rhodesia, Manitoba, Madagascar, and Transvaal)

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ABSTRACT

The lead-age distribution ($\frac{206}{238}$, $\frac{207}{235}$, $\frac{208}{232}$, and $\frac{207}{206}$) of three specimens of Rhodesian monazite form a regular pattern. Such an array, produced evidently by varying lead loss*, may be used for a precision estimate of age—the *convergent* age. The convergent age of each Rhodesian monazite is estimated at 2,680 $\times$ 10^6 years. The lead-age distributions of monazite from Antsirabe, Madagascar, and uraninite from the Huron Claim, south-eastern Manitoba, fit an extension of Rhodesian age pattern closely ($\pm$20 $\times$ 10^6 years) and hence their convergent ages are estimated also at 2,680 $\times$ 10^6 years; uraninite from Klerksdorp, Transvaal, may have a similar age. The convergent ages of those most primitive specimens are somewhat greater (50–700 $\times$ 10^6 years) than previously recommended estimates.

The formation of a well-ordered age array suggests that physical causes, rather than chemical, have controlled lead loss.

Introduction

The great antiquity of pegmatites from south-eastern Manitoba and Rhodesia has been discussed respectively by Holmes (1948), Ahrens (1948, 1955), Collins, Farquhar, and Russell (1954), Ahrens and McGregor (1952), and Holmes (1954). In the last paper Holmes (1954) presents complete data (chemical and isotope analysis) on three specimens of monazite on the basis of which he concludes that Pb loss is the chief cause for the discrepant age distribution ($\frac{206}{238}$, $\frac{207}{235}$, $\frac{208}{232}$, and $\frac{207}{206}$) for two of the monazites, and that therefore the $\frac{207}{206}$ measurements should be the most reliable index; age agreement in the third specimen is so close that no significant loss (or gain) of parent or daughter has apparently taken place. The main purpose of the present paper is to present graphically the age distribution pattern of the three Rhodesian monazites and in so doing to demonstrate the possibility of what appears to be an extremely precise method for calculating primitive age. The Rhodesia age pattern will serve as the basis for comparing the age of Rhodesian monazite with that of uraninites from south-eastern Manitoba and Klerksdorp, Transvaal, and monazite from Antsirabe, Madagascar.

The Age of Rhodesian Monazites

Age calculations on each of the oldest known monazites and uraninites are given in Table 1. These data are displayed graphically in Fig. 1, which relates the $\frac{207}{235}$ age (ordinate) vs. the $\frac{207}{206}$, $\frac{206}{238}$, and $\frac{208}{232}$ ages of the three Rhodesian monazites (Holmes, 1954), uraninite and monazite from south-eastern Manitoba (Holmes, 1948) and uraninite from Klerksdorp, Transvaal (Louw and Strelow, 1955). Consider first the three Rhodesian monazites (Nos. 2, 3, and 4 of Fig. 1). Age distribution in the Irumi and Jack Tins specimens is such that lead loss is likely (Holmes, 1954); the $\frac{207}{206}$ age is slightly depressed, whereas those of $\frac{207}{235}$, $\frac{206}{238}$, and $\frac{208}{232}$ are affected to a far greater extent. Degree of lead loss varies inversely with half-life of the respective parents; this relationship is referred to again

* *Note added in proof:* When used in a general sense, "loss" should be substituted by deficiency.

later in a discussion (below) on the cause of lead loss. Development of the well-ordered age array, produced evidently by varying lead loss (Irumi Hills > Jack Tin Claims > Bikita) is of equal note and indicates that the actual age of each monazite is identical. Stratigraphic considerations indicate this as quite likely (Holmes, 1954). The convergent point (no lead loss) should therefore be a precise estimate of the true age of each specimen: this age is $2{,}680 \times 10^6$ years.

The convergent age coincides almost exactly with the $\frac{207}{235}$ and $\frac{207}{206}$ ages of the Ebonite Claims specimen, which apparently has not lost a significant proportion of its lead. A trace of lead has evidently been lost, however, as indicated

Table 1. *"Age" calculations of the most primitive monazites and uraninites*

Specimens and locality	Age ($\times 10^6$ years) $\frac{206}{238}$	$\frac{207}{235}$	$\frac{208}{232}$	$\frac{207}{206}$	*Convergent*
Monazite, Ebonite Tantalum Claims, Bikita District, Southern Rhodesia	2,675	2,680	2,645	2,680	2,680
Monazite, Jack Tin Claims, north of Salisbury, Southern Rhodesia	2,260	2,470	1,940	2,650	2,680
Monazite, Irumi Hills, Northern Rhodesia	2,040	2,330	1,390	2,620	2,680
Monazite, Antsirabe, Madagascar	1,400	1,850	610	2,420	2,680
Monazite, Huron Claim pegmatite, south-east Manitoba	3,217	2,839	1,827	2,590	—
Uraninite, Huron Claim pegmatite, south-east Manitoba	1,564	1,985	1,273	2,475	2,680
Uraninite, Dominion Keeps, Klerksdorp, Transvaal	1,678	2,200	3,672	2,730	2,680–2,800

by some measurable lowering of the $\frac{206}{235}$ (5×10^6 years) and particularly the $\frac{208}{232}$ (35×10^6 years) ages; these are the most sensitive indicators of such loss (Fig. 1). Allowance for loss of a trace of lead gives $2{,}681 \times 10^6$ years for the Rhodesian monazites. This value is not inserted as a serious attempt at refinement, but only to emphasize the high precision with which convergent ages can be calculated under favourable circumstances such as in the example of the Rhodesian monazites. Precise convergent ages may presumably be estimated even if all specimens show serious lead loss, provided each age distribution participates to form a well-ordered age pattern.

Analytical error is probably only slight in the examples under consideration, as such an orderly array is otherwise hardly likely to have developed. Each Rhodesian monazite, as well as the Madagascan specimen, has been analyzed by the same analysts (see Holmes, 1954).

Although $\frac{208}{232}$ ages are included in Fig. 1, and happen there to show quite a well-defined regularity, they are quite susceptible to error (analytical + constitution of primary lead) and may be ignored if desired.

A Comparison of the Rhodesia Age with those of Huron Claim, South-eastern Manitoba; Antsirabe, Madagascar, and Klerksdorp, Transvaal

Assuming 24 per cent Rn loss, Holmes (1948) found that $\frac{207}{206}$, $\frac{206}{238}$, and $\frac{207}{235}$ ages of the Huron Claim uraninite, south-eastern Manitoba, could be restored to agree at $1{,}985 \times 10^6$ years, which at that time was taken as the most likely age. The age distribution of a specimen of monazite (Table 1) was difficult to manipulate, and a more complex loss scheme was required in order to bring about internal age agreement at an age equivalent to that of the uraninite. Strontium-age measurements (Ahrens, 1948; Ahrens and Gorfinkle, 1950; Ahrens and McGregor,

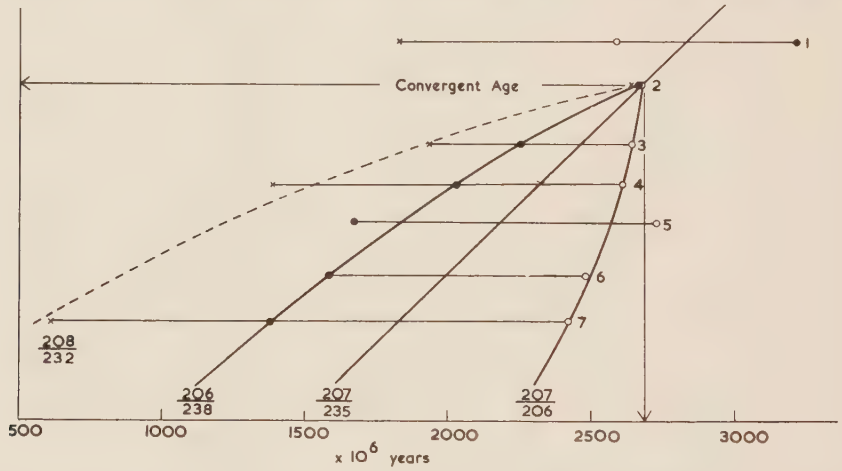

Fig. 1. The Rhodesia age pattern. 1—monazite, Huron Claim, S.E. Manitoba; 2, 3, and 4—monazites, Rhodesia (Bikita, Salisbury and Irumi, respectively); 5—uraninite, Klerksdorp, Transvaal; 6—uraninite, Huron Claim, S.E. Manitoba, and 7—monazite, Antsirabe, Madagascar.

1951; Davis and Aldrich, 1953; Nicolaysen, Aldrich, and Doak, 1953) do not indicate that the Manitoban pegmatites are quite considerably (700×10^6 years) younger than those of Rhodesia. $\frac{207}{206}$ age estimates (Table 1), which are frequently considered the most reliable for primitive specimens (Nier, 1939; Nier, Thompson, and Murphey, 1941; Collins, Farquhar, and Russell, 1954), indicate an age ($\sim 2{,}500 \times 10^6$ years) which, though slightly less, is very similar to that of Rhodesia. Holmes (1954) has recently adopted this age in place of the earlier restoration (Rn diffusion) age.

A clear comparison becomes possible, provided at least one of the Manitoban specimens shows an age distribution similar to that of the Rhodesian monazites. The age distribution of the Manitoban monazite is totally different and therefore useless for precise comparison (Fig. 1); that of the uraninite is similar, and indicates in the first place that general Pb loss, and not Rn diffusion loss, is the cause. Moreover, as the uraninite age distribution fits an extension of the Rhodesia

age pattern closely, its actual age should be either exactly equal to that of the convergent age of the Rhodesian monazite or at least very close to it. Greater spread and depression of age in the Huron Claim uraninite (Fig. 1) indicates that lead loss has been more severe than in the three Rhodesian monazites.

The Madagascan monazite from Antsirabe fits the extension of the Rhodesia age pattern closely and, as in the case of the Manitoban uraninite, the convergent age is hence estimated at $2{,}680 \times 10^6$ years. Holmes and Cahen (1954) point out that lead loss from the specimen is serious, and that although the $\frac{207}{206}$ estimate of $2{,}420 \times 10^6$ years should therefore be regarded as the most reliable, it is probably somewhat low. Fig. 1 shows clearly that lead loss in the Antsirabe specimen is indeed very serious, and considerably greater than in any of the other specimens; the reduction of the $\frac{208}{232}$ age to as little as 600×10^6 years is quite striking.

Other Madagascan ages (Nicolaysen, Aldrich, and Doak, 1953; Holmes and Besairie, 1954) are much younger than that of the Antsirabe monazite.

Louw and Strelow (1955) have published fifteen complete analyses of uraninites and carbon concentrates from different horizons within sediments of the Witwatersrand System, Transvaal. An earlier analysis was reported by Davidson (1953). One specimen (Dominion Reefs Series) appears to be distinctly older than the rest and, moreover, comes from the base of the system, immediately above the basement granite; this series appears only in the Klerksdorp (Western Transvaal) and has not been reported from the Witwatersrand (greater Johannesburg) or Odendaalsrus (Orange Free State) areas. Louw and Strelow suggest a magnitude of $2{,}200 \times 10^6$ years for the Dominion Reefs specimen, as compared with $\sim 1{,}850$–$1{,}950 \times 10^6$ years for other uraninites of the Witwatersrand System. Such ages are for the most part restoration ages based mainly on assumed Rn-diffusion loss, which usually is considered to amount to ~15–20 per cent and which in the Dominion Reefs specimens is estimated at ~28 per cent. In this discussion Holmes' Rn-diffusion restoration age ($1{,}985 \times 10^6$ years) for Huron Claim uraninite is referred to as an example. The evidence above, however, indicates strongly that the Huron Claim age is virtually identical with that of the Rhodesian pegmatites ($2{,}680 \times 10^6$ years) and that the age distribution is due to general Pb loss and not specifically to Pb^{206} loss caused by Rn-diffusion loss. The age distribution of the Dominion Reefs specimen (Fig. 1) is likewise typical of Pb loss; in which case the $\frac{207}{206}$ age of $2{,}730 \times 10^6$ years should be the most reliable magnitude. An approximate convergent age, based on the Rhodesia pattern, would be somewhat greater, namely, $\sim 2{,}800 \times 10^6$ years. It is quite likely, however, that the true (convergent) age is slightly different. Louw and Strelow estimate radiogenic lead at 93 per cent, and thus, although rock lead is comparatively low, its composition must be accurately known for a precise estimate. Louw and Strelow emphasize this difficulty, and point out that their choice of East Geduld galena ($Pb^{204} = 1{\cdot}00$, $Pb^{206} = 18{\cdot}35$, $Pb^{207} = 16{\cdot}34$, and $Pb^{208} = 34{\cdot}48$) for the purpose of attempting a correction is purely arbitrary. Such a galena constitution is typically young (cf. Fig. 9.2 of Faul, 1954), and it does not seem likely that primitive rock-lead of the order of $2{,}000 \times 10^6$ years old or greater is likely to have had this composition. Louw (personal communication) has recalculated the age of the Dominion Reefs specimen on the basis of

the lead-isotope constitution of some primitive galenas (Rosetta Mine, Barberton, Transvaal; Leopard Mine, Lower Gwelo, Southern Rhodesa; Doornhoek, Marico, Transvaal) and finds, however, that the ages are not altered appreciably. The $\frac{206}{238}$ and $\frac{207}{206}$ ages could be made to fit the general Rhodesia pattern by assuming radon diffusion loss which would have elevated the $\frac{207}{206}$ age, depressed the $\frac{206}{238}$ age, and left the $\frac{207}{235}$ age where it is. It would be unwise, however, to speculate further about the precise age of the Dominion Reefs specimen until further data are available: the specimen is evidently primitive and appears to have about the same age as, or is slightly older than, that of Rhodesia-Manitoba.

If the age of the Dominion Reefs specimen is indicative of that of the underlying basement granite, it points to a considerable southward extension of the primitive basement mass identified in Rhodesia. Strontium ages of Letaba (Transvaal) lepidolite (Nicolaysen, Aldrich, and Doak, 1953) and Kubuta (Swaziland) lepidolite (Ahrens, 1948) are apparently similar in magnitude to the strontium ages of Rhodesian lepidolites, and may perhaps serve as a guide for defining the extent of this primitive mass. It will be recalled that the Pb and Sr ages (Holmes and Cahen, 1955; Ahrens, 1948; Nicolaysen, Aldrich, and Doak, 1953) of western exposures (Namaqualand and South-west Africa) of basement granites—or rather their pegmatites—as well as those from Mozambique (Holmes and Cahen, 1955; Nicolaysen, Aldrich, and Doak, 1953) are much younger, often less than a half to a third of the Rhodesian pegmatite ages.

The convergent-age estimates provide support to the suggested possibility (Ahrens, 1955, and earlier papers) already indicated by cruder measurements, that the oldest pegmatites and their associated granites of some of the principal shield areas have precisely the same age. According to Wilson (1949 and other papers), these would be the primary nuclei about which the main continental masses developed.

Brief Comment on the Cause of Lead Loss

Although general lead loss has not been proved, the evidence strongly supports this possibility, and for the sake of further discussion such loss will be assumed to have taken place and in varying degrees. Three points should be distinguished in the discussion on the cause of lead loss; first, the general qualitative nature of the distribution ($^{207}_{206}$ age $> ^{207}_{235} > ^{206}_{238} \gg ^{208}_{232}$) in each specimen; second, the quantitative relationship between these ages; and, third, the participation of each age distribution in a well-ordered age array. It is immaterial whether we consider the three Rhodesian monazites only or include Madagascan monazite and Manitoban uraninite.

The usually suggested cause for general loss is leaching, or perhaps "reworking," and some qualitative support for such a mechanism could perhaps come from the relationship between the half-lives of the respective parent isotopes ($Th^{232} > U^{238} > U^{235}$) and the Pb loss-order ($Pb^{208} > U^{206} > U^{207}$). Other evidence seems strongly against leaching or "reworking" as the cause for lead loss, at least for the specimens under consideration. In the first place, leaching would presumably influence uranium (and thorium) as well and change the age distribution to some extent, or even alter it completely (cf. Huron Claim age distribution with others of Fig. 1);

second, leaching or "reworking" is likely to have taken place at different times, and in either case such a well-ordered array could not develop. Moreover, although lead loss may lower the thorium age greater than others, the magnitude of such an age depression seems far too great, and in the Madagascan sample would indicate that some 80 per cent was lost. Some mineralogical evidence is also difficult to reconcile with a postulate of lead loss by leaching; thus, for example, monazite crystals from the Irumi Hills are described as clear and apparently unweathered (Holmes, 1954), yet this specimen appears to have lost a considerable proportion of its lead. Monazites are rarely if ever metamict.

The well-ordered array of Fig. 1 suggests control of lead loss by physical processes which perhaps have operated at varying degrees but at a uniform rate ever since the minerals were formed. The differential lead loss ($208 > 206 > 207$) is not simply related to diffusion loss of emation (thoron, radon, and actinon) which would depend on half-life alone (Wickman, 1942; Kulp *et al.*, 1954) in which case only Pb^{206} is likely to have been lost; nor is it apparently simply related to the magnitude of the recoil energy either of parent or emanation itself both of which indicate a different lead loss order. Possibly both factors could combine to bring about the regular array of Fig. 1. Moorbath (1955) points out that properties such as ionic radius and charge of immediate parents (perhaps even earlier members of the decay chain), should also be considered, as they may influence the ultimate history of emanation. No attempt will be made to pursue this point further here. The primitive lead-loss pattern of Fig. 1 evidently requires careful consideration, and fresh data, including Pb^{210} ages, on further suites of very old and carefully selected specimens should be most helpful.

Although the same *proportion* of lead can perhaps be lost from specimens younger than those from Rhodesia-Manitoba, etc., the absolute magnitude of the effect is never so great, because smaller quantities of lead are involved. This makes the really primitive specimens particularly valuable guides for an examination of the cause of the lead-age distribution: not only is the true age distribution in younger specimens likely to be disturbed to a greater extent because analytical error assumes proportionately greater significance, but young specimens are particularly prone to serious error, which can be introduced through an unsatisfactory correction for the presence of primary lead. Significant lead loss from at least five of the specimens of Table 1 indicates that such loss is likely to have taken place in a high proportion of all monazites and uraninites. It will be recalled that many age distributions are qualitatively similar to those of Fig. 1.

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